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# Generation of thermal strains in GRP

## Part 1 *Effect of water on the expansion behaviour of unidirectional glass fibre-reinforced laminates*

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The temperature dependence of the linear expansion coefficients in the longitudinal ($\alpha_l$) and transverse directions ($\alpha_{t_1}$ and $\alpha_{t_2}$) of unidirectional glass fibre laminates and their matrix resins ($\alpha_m$) has been studied. The results for the dry, fully post-cured polyester, epoxy resins and laminates have been found to be consistent with the predictions of the Schapery equations. An anomalous moisture phenomenon, in the form of a peak in the $\alpha_m(T)/T$ and $\alpha_t(T)/T$ curves for the polyester resin and laminates has been observed. A difference between $\alpha_{t_1}$ and $\alpha_{t_2}$ has been observed for partially cured polyester laminates, which is also perturbated in the presence of water. Both these moisture effects, which are not found in the epoxy specimens, are considered to result from a two-phase polyester matrix and the latter to continued curing below the softening point of the resin. These results have a considerable consequence on the magnitude of the thermal strains which develop in polyester composites.

## 1. Introduction

The evaluation of the thermal response of composite materials is important for applications at high and low temperatures as well as in the choice of the curing temperature for fabrication. Thermal strains are always present in composite laminates exposed to a temperature regime. For a unidirectional laminate they are present at the microstructural level because of the mismatch between the thermal expansion coefficients of the fibres and matrix. For cross-ply laminates, in which the fibres in each ply are oriented at an angle to each other such strains are due to the mismatch between the thermal expansion coefficients of plies of different orientation. Furthermore, these tensile thermal strains can reduce the applied strain at which the matrix debonding and transverse cracking occurs [1, 2].

Various measurements of the thermal strains generated in carbon and glass fibre-reinforced epoxy [1, 2] and polyester [3, 4] based cross-ply laminates have been made. On comparing these results it was observed that the measured thermal strains in glass fibre-reinforced polyester laminates were considerably larger than those developed in similar laminates made from an epoxy resin. This difference was surprising in view of the fact that the epoxy resin based laminates were post-cured at a higher temperature and the heat distortion, or glass transition, temperature of the epoxy resin was also higher than that of the polyester. This implied that the expansion coefficient of the polyester resin was larger than that of the epoxy resin.

In this paper we report a study of the thermal expansion behaviour of unidirectional glass fibre laminates, their matrix resins and the effect of the post-curing schedule. The experimental results have been compared with the theoretical predictions of Schapery [5]. The linear expansion coefficients which have been calculated at different temperatures have highlighted an anomalous thermal expansion behaviour of the polyester resin in the presence of small quantities of water. The significance of this result in explaining the anomalous thermal strains in polyester laminates is discussed elsewhere [6].

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## 2. Experimental details

### 2.1. Materials

The materials selected for this study were Crystic 272 (Scott-Bader and Co. Ltd.) and Epikote 828 (Shell Co. Ltd.) since E-glass fibre-reinforced composites incorporating these resins have been studied extensively [1–4].

Crystic 272 is an isophthalic unsaturated polyester resin and was cured using 2 phr (parts per hundred of resin) of a 50% methyl ethyl ketone peroxide solution (catalyst M) and 0.25 phr of a cobalt naphthenate solution (Accelerator E, Scott-Bader and Co. Ltd.). At this concentration of accelerator the resin has a relatively long gelation time of 6 to 12 h with a negligible increase in temperature. Slow gelling formulations have been used to fabricate reproducible, void free laminates. The expansion coefficients of samples cured with up to 1 phr of accelerator were slightly smaller. However, at a concentration of 1.0 phr the gel time is reduced to about 1 h and in sections thicker than about 20 mm this produced a significant exotherm with a consequent lack of control of the cure.

All of the polyester samples were allowed to cure at room temperature for at least 24 h prior to post-curing. In this study three standard post-cure schedules were used: (i) 15 h at 50° C, (ii) 3 h at 80° C, (iii) 1.5 h at 130° C. A resin subjected to schedule (iii) is considered to be fully post-cured.

Epikote 828 is a Bisphenol 'A' epoxy resin and was cured with 80 phr nadic methylene anhydride (NMA) and 1.5 phr benzyl dimethylamine (BDMA). Unlike the polyester system the epoxy does not cure at room temperature and therefore was cured at 100° C for 3 h, which was in some cases followed by post-curing for 3 h at 150° C.

The glass fibres used in the laminates were Silenka 051P 1200 tex 'E' glass fibres with a silane finish compatible with polyester and epoxy resins. The fibres are supplied as a roving in the form of a flat tape containing approximately 4000 fibres, the fibre diameter was in the range 10 to 12 $\mu$m.

### 2.2. Specimen preparation

#### *2.2.1. Pure resin*

Specimens of the polyester of a convenient shape and size were obtained by casting the activated resin into 8 mm diameter pyrex glass tubes, 50 mm in height. After 24 h at room temperature the cured resin was cut into lengths of between 7 and 8 mm using a water cooled rotary diamond wheel. The epoxy resin specimens were prepared in a similar manner but curing was accomplished by heating for 3 h at 100° C.

#### *2.2.2. Unidirectional laminates*

Undirectional laminates were made by machine winding individual plies of glass rovings onto square steel frames, 400 mm × 400 mm made from strips 25 mm wide and 2 mm thick spot welded at each corner.

For the polyester resin impregnation of the fibres was achieved by pouring activated resin onto a "Melinex" sheet supported on a glass plate 300 mm square and 5 mm thick. The frame was then placed over the glass plate causing the resin to wet the fibres. A second Melinex sheet was then placed over the frame and any remaining entrapped air was removed by wiping the release film with a plastic spatula. Once the glass fibres were fully wetted out a second glass plate was placed on top and a pressure of 10 kPa applied. The laminate was then allowed to cure for 24 h at 20° C. In a control experiment a thermocouple was embedded in the laminate and, with the accelerator level used, there was no measurable exotherm. This technique produced 2 mm thick unidirectional laminates, 200 mm wide and 250 mm long, with a volume fraction of 34 ± 2% as measured by three separate techniques (Section 2.4).

The epoxy resin laminates were prepared using an elevated temperature vacuum assisted impregnation technique [7]. At 100° C the epoxy resin formulation has a lower viscosity than the polyester resin so that a volume fraction of 55 ± 5% was achieved. The laminate was cured at 100° C for 1.5 h.

Once cured the laminates, both polyester and epoxy based, were cut from the metal frames using a water cooled rotary diamond wheel. Test specimens 10 mm × 8 mm were then cut from the unidirectional sheets. Specimen thickness was approximately 2 mm depending on the volume fraction of the individual laminate.

After post-curing, on a metal plate in an air circulating oven with temperature control to ± 1° C, the resin and laminate specimens were stored in a desiccator prior to testing.

### 2.3. The determination of expansion coefficients, $\alpha$

The thermal expansion behaviour of both the

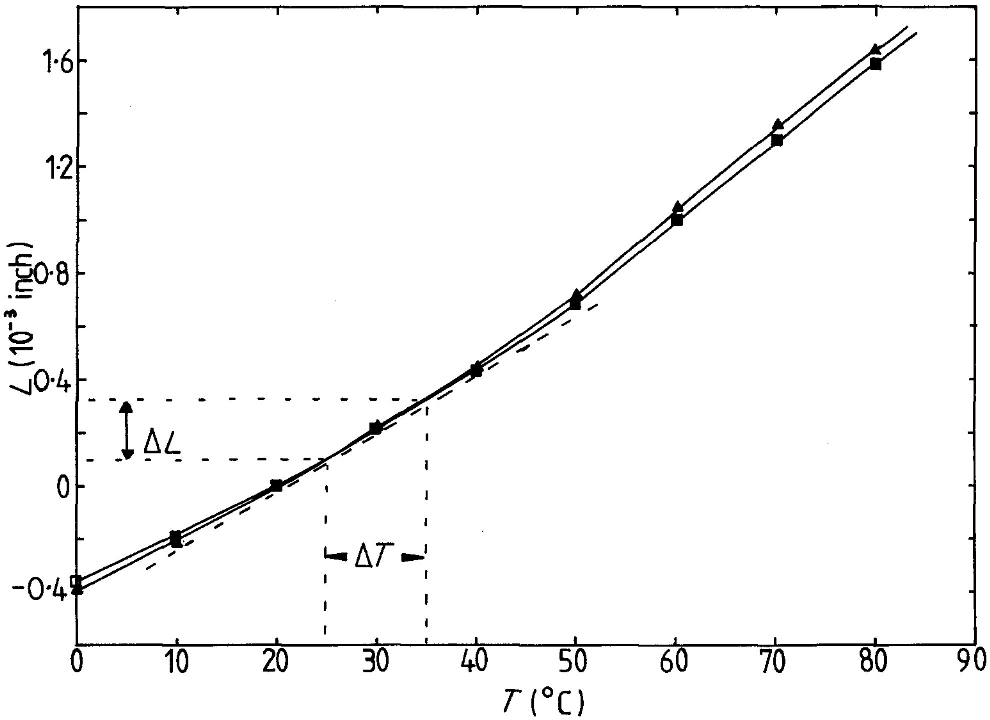

*Figure 1* The probe displacement ($L$) – temperature ($T$) curves for the polyester resin (post-cured at 130° C for 1.5 h), (a) 1st cycle (▲) (b) 4th cycle (■). The dashed line is parallel to a chord between points on the curve at $T \pm 5°$ C where $T = 30°$ C showing $\Delta L$ and $\Delta T$.

resin and laminates was studied, where possible, over the temperature range $-50$ to 150° C using a Dupont 942 Thermomechanical Analyser (TMA). This produces a trace of change in specimen length, $L$, as a function of specimen temperature $T$, which we refer to as a thermogram. A heating rate of 2° C min$^{-1}$ was found to eliminate specimen size effects. During measurements the apparatus was flushed with oxygen free nitrogen to eliminate possible oxidation effects and to establish reproducible conditions.

Calibration of the apparatus was carried out using a standard block of aluminium of known expansion coefficient ($\alpha = 23 \times 10^{-6} \mathrm{K}^{-1}$). As a further check base-line measurements were made by running the apparatus in the absence of a sample. This revealed a slight positive bias which represented an error of $+2.5 \times 10^{-6} \mathrm{K}^{-1}$ over the temperature range considered.

The effect of specimen size on the results was investigated by examining resin specimens of differing nominal diameters (5, 8, 10 and 11 mm). All four were found to have identical values of expansion coefficient provided the heating rate was 0.5° C min$^{-1}$ or less. In practice the 8 mm diameter specimen was used since the tube was easily filled with resin and a heating rate of 2° C min$^{-1}$ could be used. All the samples, cut from a single cast rod, were found to have the same expansion coefficient, within experimental error, demonstrating the homogeneity of each casting.

In most cases the $L/T$ thermograms had a reproducible curvature demonstrating that the expansion coefficient, $\alpha$, was a function of temperature. We established that, providing the test temperature did not exceed the post-cure temperature or the softening point of the cold-cured samples, a reproducible thermogram could be obtained on the same sample. A typical result is given in Fig. 1 for a sample post-cured at 130° C and subjected to 4 heating cycles. For sake of clarity we only show the first and final runs, where a maximum difference exists. In practice a similar difference existed between the first and second cycles and subsequent runs were identical. The maximum difference is small and represents an error of 4% in the calculated value of $\alpha_m$. The thermograms from individual specimens were of similar reproducibility and as such a set of curves is not included here since they lay on top of each other. The results presented here as linear

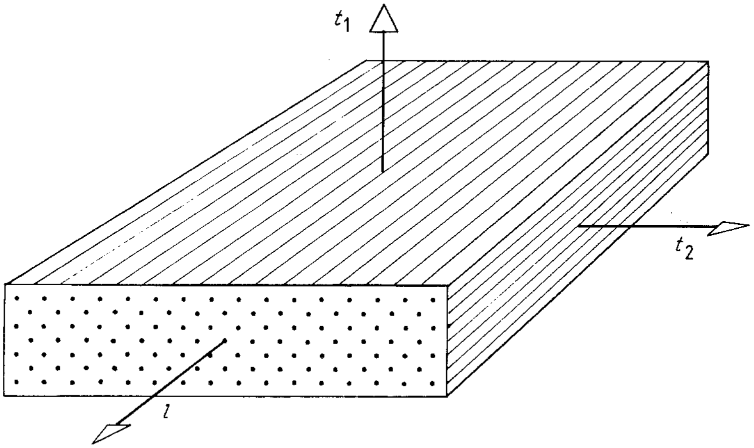

*Figure 2* Model specimen of unidirectional laminate showing the longitudinal and two transverse directions.

expansion coefficients are averages of at least 5 individual samples whose reproducibility was ± $5 \times 10^{-6}\,\mathrm{K}^{-1}$ which is considered the error in the technique.

The expansion coefficient at some temperature, $T$ is given by Equation 1

$$\alpha(T) = \frac{1}{L_\mathrm{T}}\frac{\mathrm{d}L}{\mathrm{d}T} \tag{1}$$

where $L_\mathrm{T}$ is the length at temperature $T$.

In practice it is difficult to accurately draw a tangent to the curve at $T$ and we have therefore obatined the first derivative of the thermogram by constructing chords on the curve between $(T + 5^\circ\,\mathrm{C})$ and $(T - 5^\circ\,\mathrm{C})$. At these increments $\Delta L/\Delta T$ (Fig. 1) approximates to $\mathrm{d}L/\mathrm{d}T$.

The pure resin specimens were found to be isotropic so that we present only a single value of the expansion coefficient at any temperature $T$, defined as $\alpha_\mathrm{m}(T)$. For the unidirectional laminates we have measured three different expansion coefficients. A longitudinal value measured parallel to the fibre axis, $\alpha_\mathrm{l}(T)$ and two transverse values perpendicular to the fibre axis, one through the thickness, $\alpha_{\mathrm{t}_1}(T)$ and the other in the plane of the composite $\alpha_{\mathrm{t}_2}(T)$ (see Fig. 2).

For the epoxy laminates so measurable difference between $\alpha_{\mathrm{t}_1}(T)$ and $\alpha_{\mathrm{t}_2}(T)$ was found but in the lower volume fraction polyester laminates a significant difference which decreased with increasing post-cure temperature, was observed.

## 2.4. The determination of fibre volume fraction ($V_\mathrm{f}$)

The volume fraction of the unidirectional laminates was determined using three separate techniques: (a) density measurements; (b) thickness measurements; and (c) thermal decomposition of the resin.

### *2.4.1. Density measurements*

The fibre volume fraction in a unidirectional void-free laminate is directly related to the density of the laminate, fibres and matrix by the relationship

$$V_\mathrm{f} = (\rho_\mathrm{c} - \rho_\mathrm{m})/(\rho_\mathrm{f} - \rho_\mathrm{m}) \tag{2}$$

If the densities of the fibre, $\rho_\mathrm{f}$ and resin $\rho_\mathrm{m}$ are known then $V_\mathrm{f}$ can be calculated from the laminate density, $\rho_\mathrm{c}$.

The density of the specimens were obtained by measuring the dimensions of each with a micrometer and weighing them using an analytical balance. This method was found to be more comvenient and less problematical than the use of a density bottle or similar technique.

### *2.4.2. Thickness measurements*

During the winding of the fibres onto the frames a known number of tows, $C$, were laid down over a given width. For a laminate containing $N$ plies the fibre volume fraction is related to the thickness, $t$, by the relationship

$$V_\mathrm{f} = NCF/t\rho_\mathrm{f} \tag{3}$$

where $F$ = fibre weight per metre.

Measurements of laminate thickness (through the plane of lamination) and knowledge of $N$, $C$, $F$ and $\rho_\mathrm{f}$ enable the volume fraction of each specimen to be determined.

### *2.4.3. Thermal decomposition of the resin*

Laminate specimens of known weight were heated for 3 h at 600° C in preweighed ceramic crucibles. They were reweighed after cooling in a desiccator.

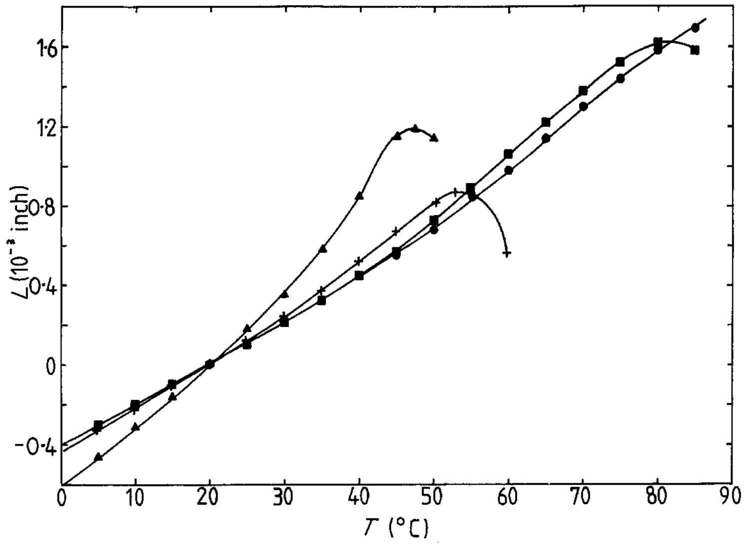

*Figure 3* The probe displacement – temperature ($L/T$) thermograms for the polyester resin given different post-curing schedules, (a) None (▲), (b) 15 h at 50° C (+), (c) 3 h at 80° C (■), (d) 1.5 h at 130° C (●).

From the known weights of the laminate $w_c$ and the remaining fibres $w_f$, the weight fraction of fibres, $W_f$ was calculated from Equation (4)

$$W_f = w_f/w_c. \tag{4}$$

From the densities of the matrix and the fibres the fibre volume fraction $V_f$ can be computed from Equation 5

$$V_f = (w_t/\rho_f)/[(w_f/\rho_f) + (w_m/\rho_m)] \tag{5}$$

where

$$w_m = w_c - w_f.$$

## 3. Results

### 3.1. Resins

The probe displacement with temperature ($L/T$ thermogram) for both cold-cured and post-cured resins are reproducible providing the furnace temperature was not allowed to exceed the softening point of the resin. If the temperature is allowed to rise the resin softens and the probe displacement ($L$) becomes negative indicating either penetration by the probe, overall creep of the resin block or further post-curing. There was no detectable variation in the dimensions of the cooled sample nor evidence of probe penetration to the naked eye. For the purpose of our discussion we define the softening point of the partially cured resin as the maximum in the $L/T$ thermogram. For fully post-cured polyesters (130° C) and the epoxy resins a change in gradient, consistent with a glass transition, rather than a maximum is observed, It is clear, therefore, from Fig. 3 that the softening point is larger at higher post-curing temperatures. In Fig. 4, the thermo-

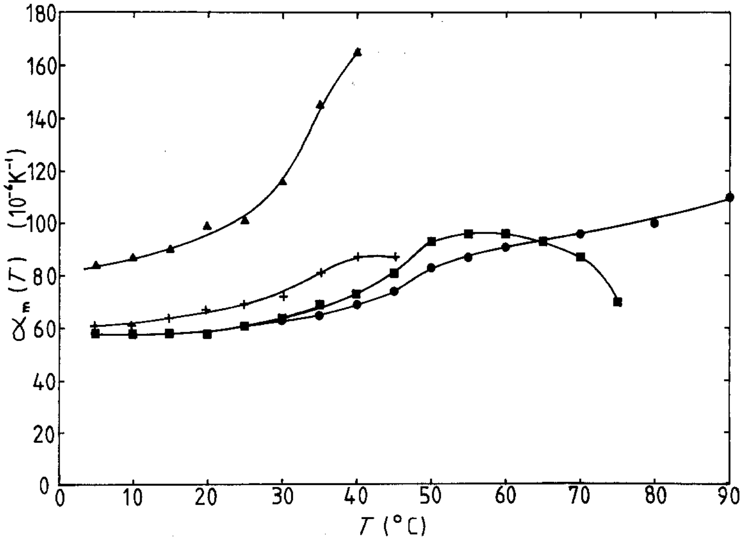

*Figure 4* The linear expansion coefficients $\alpha_m(T)$ of the polyester resin as a function of temperature $T$, obtained from the data in Fig. 3. (a) no post-curing (▲), (b) 15 h at 50° C (+), (c) 3 h at 80° C (■), (d) 1.5 h at 130° C (●).

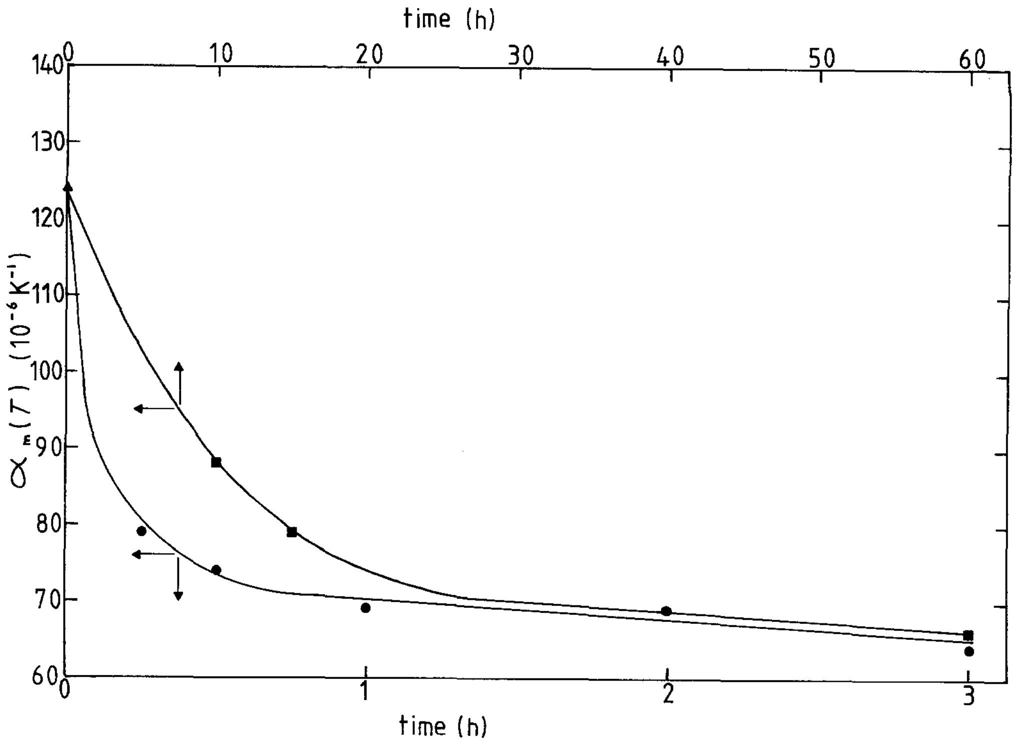

*Figure 5* The time dependence of $\alpha_m(30)$ during the post-curing of the polyester resin at 50° C (■) and 80° C (●).

grams have been converted into $\alpha_m(T)/T$ curves where it can be seen that at any given temperature $T$, $\alpha_m(T)$ decreases with the post-curing temperature. The method of differentiation given in Section 2.3 gives accurate values of $\alpha_m(T)$ up to 5° C below the softening point of the resin so that the reduction in $\alpha_m(60)$ for the 80° C post-cured resin is a real effect. For samples which are less than "fully" post-cured some further curing might be expected during the recording of an $L/T$ thermogram. However, the decrease of $\alpha_m(30)$ with time at two different post-curing temperatures, given in Fig. 5, demonstrates that the rate of post-curing below 50° C is sufficiently low so that a negligible effect can be expected during the time scale of the measurements.

It is significant that $\alpha_m(30)$ reaches a value of $66 \times 10^{-6}$ after 60h at 50° C and 3h at 80° C. The softening point, after 60h at 50° C, had also increased above 50° C demonstrating that the curing reactions are able to continue within the glass. Furthermore, it was observed that the cold-cured resin samples continued to cure on storage at room temperature as shown by a decrease in $\alpha_m(30)$ from 127 to $105 \times 10^{-6}\,K^{-1}$ over 4 weeks.

The experiments were carried out within 5 days of post-curing (the samples were stored in a desiccator prior to testing). It was surprising, therefore, when resin samples, which had been stored in air for several days prior to testing showed anomalous behaviour and the presence of a peak at 70° C in the $\alpha_m(T)/T$ curve similar to that given in Fig. 6.

Since similar behaviour of epoxy resins has been attributed to plasticization by water [8] the $\alpha_m(T)/T$ curves for fully post-cured samples of both resins, immersed in distilled water for 2 days, were obtained. Fig. 6 gives these results showing the formation of a peak in the $\alpha_m(T)/T$ curve for the polyester resin, corresponding to a significant increase in $\alpha_m(T)$ below 90° C. Also included in Fig. 6 is the trace for a sample subjected to isothermal heating at 100° C for 5h, where the $\alpha_m(T)/T$ curve is shown to return to its original form. Results for the epoxy (Fig. 6) show that post-curing increases the glass transition temperature, as shown by a shift of the rapid increase in $\alpha_m(T)$ to higher temperatures. Below 100° C the value of $\alpha_m(T)$ is not noticeably affected by either post-curing or immersion in water for periods of up to one week.

## 3.2. Laminates

A difference between the values of $\alpha_{t_1}(T)$ and

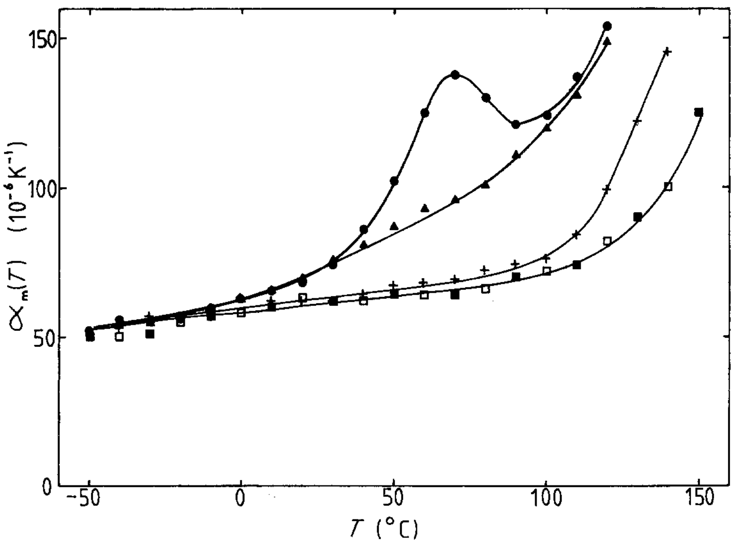

*Figure 6* The effect of immersion in distilled water for 2 days on the values of $\alpha_m(T)$ for the epoxy resin post-cured at 100° C (+) and 150° C (dry □, wet ■) and polyester resin post-cured at 130° C (dry ▲, wet ●).

$\alpha_{t_2}(T)$ (see Fig. 2) was observed for the cold-cured polyester laminates and those which had been post-cured at 50° C. The latter results are shown in Fig. 7 together with the values of $\alpha_l(T)$. This difference between the expansion coefficients in the $t_1$ and $t_2$ directions was absent in laminates post-cured at 130° C. None of the epoxy laminates showed this effect. It is not possible to explain these results in terms of resin-rich layers at mould surfaces, since calculation shows that for an average value of $\alpha_{t_1}(T)$ these layers would need to be $\simeq 0.1$ mm thick and this is not consistent with microscopic observations. However, we have shown in Section 3.1 that the polyester resin continues to cure below its softening point. It appears, therefore, that during the preparation of the laminate in which the $t_1$ direction is under load, a compressive strain can be built in, with the result that $\alpha_{t_1}$ includes an additional expansion component caused by its thermal relaxation and is consequently larger than $\alpha_{t_2}$. After immersion in water $\alpha_{t_2}$ is increased in a similar manner to $\alpha_t$ for the fully post-cured laminate shown in Fig. 8. On the other hand $\alpha_{t_1}$ is reduced but this is consistent with plasticization of the resin and relief of the compressive strain in the $t_1$ direction.

In Figs. 9 and 10 the values of $\alpha_t(T)$ and $\alpha_l(T)$ for the polyester and epoxy resins post-cured at 130 and 150° C, respectively, are shown. Also included in these figures are the theoretical values of $\alpha_t(T)$ and $\alpha_l(T)$ calculated from the equations of Schapery [5]. The laminate properties used in the calculations are given in Table I.

The anomalous moisture effect observed for the polyester resins (Fig. 6) has also been observed in the values of $\alpha_t(T)$ for the unidirectional glass fibre composites. Fig. 8 gives the results for the effect of moisture on the expansion behaviour of

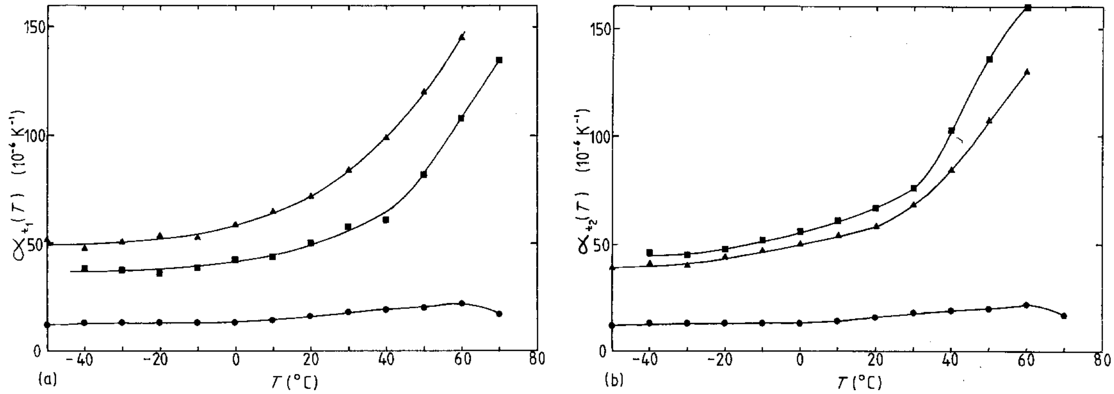

*Figure 7* The values of $\alpha_l$, $\alpha_{t_1}(T)$ and $\alpha_{t_2}(T)$ (see Fig. 2) for the polyester laminates post-cured at 50° C, as a function of temperature, $T$ before 2 days immersion in distilled water, $\alpha_l(T)$ dry ●; $\alpha_t(T)$ dry ▲; $\alpha_t(T)$ wet ■.

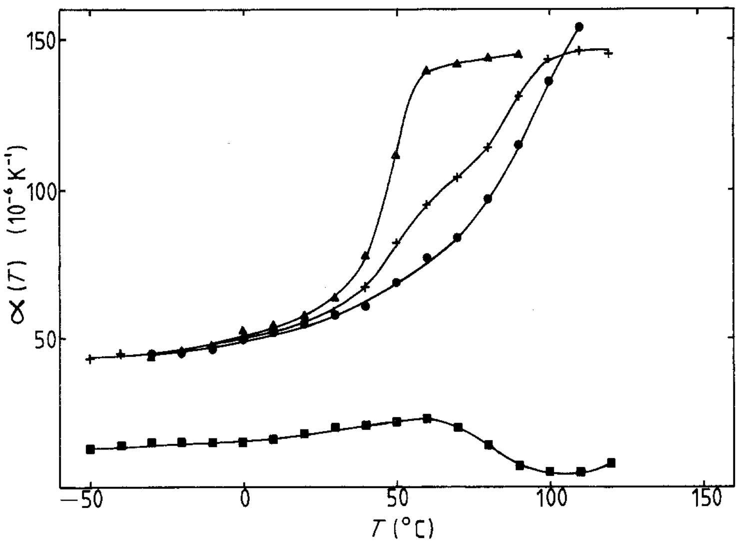

*Figure 8* The effect of immersion in distilled water on $\alpha_t(T)$ of the polyester laminates post-cured at 130° C. $\alpha_t(T)$ dry (•); $\alpha_t(T)$ 2 days (+); 28 days (▲); $\alpha_l(T)$ (■).

polyester laminates post-cured at 130° C. These were obtained by simply immersing post-cured specimens in distilled water for 2 and 28 days. It is apparent that $\alpha_t(T)$ is increased after immersion in water for 2 days. Associated with this increase in $\alpha_t(T)$ was a specimen weight gain of 0.15 ± 0.05%. On isothermal heating of the specimen at 100° C for 5 h the specimen weight and values of $\alpha_t(T)$ were found to return to those obtained prior to immersion, as was demonstrated for the resin in Fig. 6. Further immersion for 2 days produced a similar weight gain and change in $\alpha_t(T)$ values. It is of note that a similar weight increase was observed when these specimens were stored in air for 5 days.

## 4. Discussion

### 4.1. Resins

The maximum in the $\Delta L/T$ thermogram for the polyester resin is defined as the softening point. It is found to increase up to 110° C by post-curing at higher temperatures, in agreement with the results obtained by Dynamic Mechanical Thermal Analysis [13] and from the onset of curvature of an unbalanced 0°/90° cross-ply beam [6]. The maximum value of 110° C was observed for fast cooled laminates [6]. Curing at room temperature and prolonged post-curing at 50° C produced a reduction in the values of $\alpha_m(T)$ with a simultaneous increase in the softening temperature to a value in excess of the temperature seen

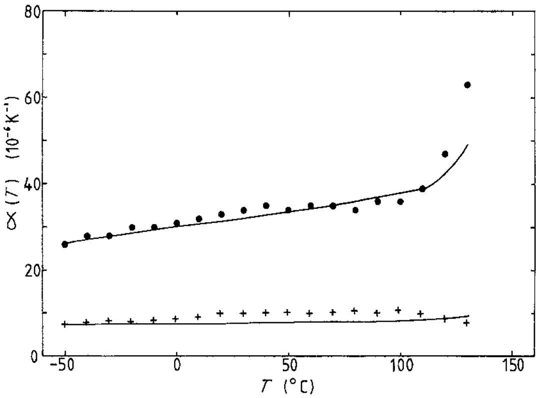

*Figure 9* A comparison of the experimental $\alpha_t(T)$, (•) and $\alpha_l(T)$, (+) for the epoxy specimens post-cured at 150° C with those calculated from the equations of Schapery [5] using the values of $\alpha_m(T)$ in Fig. 6 and the laminate data given in Table I (continuous lines).

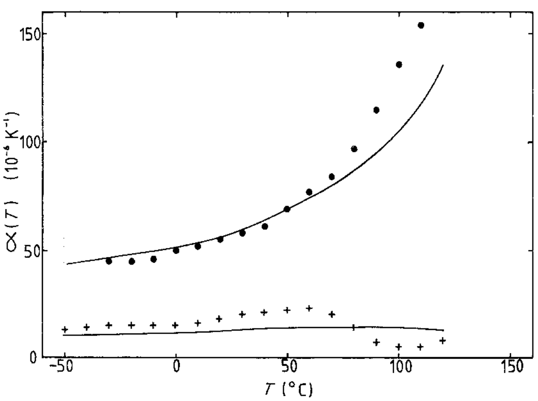

*Figure 10* A comparison of the experimental values of $\alpha_t(T)$, (•) and $\alpha_l(T)$, (+) for the polyester resin post-cured at 130° C, with those calculated from the equations of Schapery [5] using the data given in Fig. 4 and Table I (continuous lines).

TABLE I Resin and laminate properties used for the calculation of the transverse and longitudinal expansion coefficients [$\alpha_t(T)$ and $\alpha_l(T)$] from Equations 5 and 6

| Property | Polyester* | Epoxy† |
|---|---|---|
| | *Resin* | |
| $E_m$ | 4.0 GPa [4] | 3.6 GPa [2] |
| $\nu_m$ | 0.4 [9] | 0.38 [9] |
| $\alpha_m$ | (Fig. 6) | (Fig. 6) |
| | *Laminate* | |
| $V_f$ | 0.34 | 0.55 |
| $E_l$ | 1.4 GPa [4] | 42 GPa [1] |
| $\nu_t$‡ | 0.3 [1] | 0.27 [1] |
| | *Fibre* [10, 11] | |
| $E_f$ | 72 GPa | |
| $10^6 \alpha_f$ | 5 $K^{-1}$ | |
| $\nu_f$ | 0.2 [12] | |

*Post-cured at 130° C for 1.5 h.
†Post-cured at 150° C for 3 h.
‡Calculated from $\nu_t = \nu_m V_m + \nu_f V_f$.

by the resin. This result is in contrast to previous reports where the glass transition temperature ($T_g$) of a thermoset is controlled by the post-curing temperature. Gillham [14] has shown that $T_g$ is a function of the curing temperature and $T_{g\infty}$, the glass transition temperature of the fully cured resin, since vitrification is considered to immobilize the reactive components. However, the polyester resin in this study has been shown to continue curing below its softening or glass transition temperature. It has been postulated from light scattering [15], pulsed and broad line NMR spectroscopy [16] and chemical degradation [17] that these resins have a microstructure consisting of microgel particles embedded in a less densely cross-linked phase. Funke *et al.* [18] has also been able to prepare microgel particles from these and similar resins. Bergmann and Demmler [16] concluded from their NMR study that a fully post-cured resin consisted of 100 nm diameter nodules with 5 nm interstices and confirmed this with dynamic mechanical analysis, in which two relaxation temperatures, attributed to each phase, were observed. On post-curing the nodular phase grew at the expense of the interstitial material.

Since curing strains, which are relieved at higher post-curing temperatures, develop in cold-cured cross-ply laminates [4], the resin must be bonded to the glass fibres through fusible linkages. In an analogy with the domains in thermoplastic elastomers these densely cross-linked nodules can act as temporary cross-links. The implications of this model is that during continued cross-linking, below the softening point, the shrinkage of the resin matrix cannot be accommodated by molecular rearrangements within it, with the establishment of internal strains (see Section 3.2).

The peak which forms in the $\alpha_m(T)/T$ curves (Fig. 6) on absorption of water can be explained by either differential water uptake by each phase or a differential efficiency of plasticization of the two phases by the same quantity of water. The former explains the appearance of the peak in terms of a plasticized low density phase and a relatively unplasticized high density phase whereas the latter implies that the less dense phase is more efficiently plasticized by the water. It is well known that certain polymeric structures are more efficiently plasticized than others and preliminary results [13] indicate that the rate of uptake of water was not significantly different for cold-cured and post-cured samples, where the proportion of each phase might be expected to be different. Further experiments are in hand to resolve these differences but in each it is expected that plasticization by water would cause the relaxation of the internal strain state of a composite, which is shown in Fig. 7.

These phenomena have not been observed for the epoxy resin specimens or laminates which demonstrates a likely difference in the cross-linked microstructure of the matrix.

## 4.2. Laminates

Post-curing had the expected result of reducing $\alpha_t(T)$ and increasing the softening point of the resin which negated the possible inhibition of the curing reactions by the glass fibres, which could have explained the apparently high expansion coefficient inferred from the large experimental thermal strains [4].

The transverse expansion coefficients $\alpha_{t_1}(T)$ and $\alpha_{t_2}(T)$ for 50° C post-cured laminates were unexpectedly found to differ (Fig. 7). It is considered that this results from the ability of the resin to continue curing in the solid-state and has been discussed more fully in Sections 3.2 and 4.1. Water absorption has a profound effect on these transverse expansion coefficients causing $\alpha_{t_1}(T)$ to decrease and $\alpha_{t_2}(T)$ to increase. This observation is consistent with an anisotropic strain state in the dry laminates, which is partially relaxed in the presence of water.

The equations of Schapery [5] as applicable to continuous fibre unidirectional composites are given by

$$\alpha_l(T) = (E_m\alpha_m V_m + E_f\alpha_f V_f)/(E_m V_m + E_f V_f) \quad (6)$$

$$\alpha_t(T) = \alpha_m V_m(1+\nu_m) + \alpha_f V_f(1+\nu_f) - \alpha_l \nu \quad (7)$$

where, $E$, $\alpha$, $V$, $\nu$, are the Young's moduli, expansion coefficient, volume fraction and Poisson's ratio, respectively, of the matrix (subscript m), fibre (f) and composite (c).

It can be shown that these equations are special cases of the equations of Van Fo Fy [19]. Thus, theoretically, Equation 6 is only an exact solution, if $\nu_m = \nu_f$, so that the fibres and matrix do not interact under axial loading and as a result the longitudinal modulus, $E_l$, is given by the rule of mixtures, i.e. $E_l = E_m V_m + E_f V_f$. When $\nu_m \neq \nu_f$, Equation 6 can be expected to provide a lower bound to the value of $\alpha_l$.

For Equation 7, transverse isotropy of the laminate is required so that the Poisson's ratio under axial loading, $\nu_c$, can be approximated by the rule of mixtures, i.e. $\nu_c = \nu_m V_m + \nu_f V_f$. Since for the laminate considered here $\alpha_l(T)$ is relatively small, little error in $\alpha_t(T)$ is introduced by this approximation. Fig. 9 shows the results of the calculations of $\alpha_t(T)$ and $\alpha_l(T)$ for epoxy resin laminates using the values of $\alpha_m(T)$ given in Fig. 6. As can be seen there is a good agreement between the experimental values of $\alpha_t(T)$ and $\alpha_l(T)$ and those predicted by the Schapery equations. Fig. 10 gives the results of similar calculations for the dry polyester laminates. The agreement between the experimental and theoretical values of $\alpha_t(T)$ and $\alpha_l(T)$ is good but begins to deviate as the softening point of the resin is approached. The Equations 6 and 7 were derived for an elastic matrix and are consequently not applicable near the glass transition of the resin.

These equations can be used to predict the expansion and contraction behaviour of unidirectional composites over a wide temperature range, from the measured properties of the individual components. This is an important result since the deviation of the $\alpha_t(T)/T$ curve for the wet laminate shown in Fig. 8 results from an increase in $\alpha_m$ and providing the variation of $\alpha_m$ with moisture content is known the value of $\alpha_t$ can be calculated. We report the application of this principle elsewhere [6].

In Fig. 8 the effect of immersion in distilled water on the values of $\alpha_t(T)$ and $\alpha_l(T)$ for a polyester laminate post-cured at 130° C is shown. The general trend to large values of $\alpha_t(T)$ with time is clear. Comparison with Fig. 6 demonstrates that the presence of small quantities of water in the polyester matrix has a large effect on the expansion behaviour of the laminate. Thus on cooling a "wet" polyester laminate from the post-curing temperature the matrix will contract more than if it were dry, with the result that a higher thermal strain will be built in. The level of thermal strain will depend on the moisture content of the coupon, which in turn is shown in Section 3.2 to be only removed after prolonged thermal treatments.

The levels of thermal strain in 0°/90°/0° cross-ply laminates can be calculated from the curvature of an unbalanced 0°/90° beam. In a subsequent paper [6] we calculate the deflection expected from the measured values of $\alpha_t(T)$ and $\alpha_l(T)$ and compare it with the experimental curvature, and show that the anomalous thermal strains found in polyester laminates can be attributed to the anomalous moisture effect reported here.

## 5. Conclusions

The expansion behaviour of unidirectional epoxy and polyester laminates have been found to respond to post-curing in a similar manner to the resins.

The softening or glass transition temperature of the polyester and epoxy resins increased with post-curing temperature up to a maximum value. The maximum value for the former was found to be 110° C whereas that of the latter was controlled by the post-curing schedule. The linear expansion coefficient $\alpha_m(30)$ of the polyester resin has been found to be reduced to a limiting value of $66 \times 10^{-6}\,\mathrm{K}^{-1}$ during post-curing. Of particular note is the continued reduction of $\alpha_m(30)$ and increase in the softening point over 60h at 50° C, showing that the curing reactions still continue within the glassy resin.

The expansion coefficients of the fully post-cured (130° C) polyester and epoxy resins $\alpha_m(T)$ and laminates $\alpha_t(T)$ and $\alpha_l(T)$ are entirely self consistent as shown by a good agreement between the measured and calculated values based on the equations of Schapery [5]. However, the transverse expansion coefficients ($\alpha_{t_1}$ and $\alpha_{t_2}$) of partially post-cured (50° C) polyester specimens are found to differ and do not lend themselves to analysis by these equations. A likely explanation is that internal strains result from the continued curing of the resin in the solid state. This is consistent with the reports [15–17] that polyester resins have a microstructure consisting of both low and high density cross-linked phases. Immersion in water had no measurable effect on $\alpha_m(T)$ of the epoxy resin but small quantities of water of the order of 0.15%, which are not easily removed from the specimen, are responsible for a peak in the $\alpha_m(T)/T$ and $\alpha_t(T)/T$ curves of the polyester resins and laminates. It is postulated that the two resin phases are differentially placticized by water. This anomalous moisture phenomenon increases the contraction of the matrix on cooling from the post-curing temperature and can result in larger thermal strains in the composite.

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## References

1. J. E. BAILEY, P. T. CURTIS and A. PARVIZI, *Proc. Roy. Soc. Lond.* **A366** (1979) 599.
2. J. E. BAILEY and A. PARVIZI, *J. Mater. Sci.* **16** (1981) 649.
3. J. E. BAILEY, T. M. W. FRYER and F. R. JONES, "Advances in Composite Materials" Vol. 1, edited by A. R. Bunsell, C. Bathias, A. Martrenchar, D. Menkes and G. Verchery (Pergamon, Paris, 1980) p. 514.
4. F. R. JONES, A. R. WHEATLEY and J. E. BAILEY, "Composite Structures", edited by I. H. Marshall (Applied Science, London, 1981) p. 415.
5. R. A. SCHAPERY, *J. Comp. Mat.* **2** (1968) 380.
6. F. R. JONES, M. MULHERON and J. E. BAILEY, *J. Mater. Sci.* 18 (1983) 1533.
7. F. R. JONES, J. W. ROCK and J. E. BAILEY, *ibid.* 18 (1983) 1059.
8. R. De IASI and J. B. WHITESIDE, "Advanced Composite Materials – Environmental Effects" ASTM STP658, edited by J. R. Vinson (American Society for Testing and Materials, Philadelphia, 1978) p. 2.
9. D. B. S. BERRY, B. I. BUCK, A. CORNWELL and L. N. PHILLIPS, "Handbook of Resin Properties, PART A: Cast Resins" (Yarsley Testing Laboratories, UK, 1975).
10. J. KLUNDER, "Service Manual on Glass Fibres" (NV Silenka, Holland, 1970) p. 17.
11. *Idem,* private communication.
12. J. E. ASHTON, J. C. HALPIN and P. H. PETIT, "Primer on Composite Materials: Analysis" (Technomic, Stamford 1969).
13. F. R. JONES and M. MULHERON, "Proceedings of the Conference on Crosslinking and Network Formation in Polymers" (Plastics and Rubber Institute, London, 1982) p. 29.
14. J. K. GILLHAM, "Developments in Polymer Characterisation – 3", edited by J. V. Dawkins (Applied Science, London, 1982) Chap. 5.
15. L. GALLACHER and F. A. BETTELHEIM, *J. Polym. Sci.* 58 (1962) 697.
16. K. BERGMANN and K. DEMMLER, *Koll. Z. Z. Polym.* **252** (1974) 204.
17. W. FUNKE, *J. Polym. Sci.* **C16** (1967) 1497.
18. W. FUNKE, R. KOLITZ and W. STRAEHLE, *Makromol. Chem.* **180** (1979) 2797.
19. G. A. VAN FO FY, *Sov. Phys. Dokl.* **11** (1966) 176. Translation of *Dokl. Akad. Nauk. SSSR* **166** (1965) 817.

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