Generation of thermal strains in GRP

Part 2 *The origin of thermal strains in polyester cross-ply laminates*

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The temperature dependence of the thermal strains in the longitudinal direction of the transverse ply ϵ_{tl}^{th}, of $0°/90°/0°$ epoxy and polyester laminates, has been determined from the thermal variation of the deflection of an unbalanced beam. These results have been compared with those predicted from known values of the linear expansion coefficients, α_t and α_l. There is good agreement between the experimental and calculated values of thermal strain for the epoxy composite. Good agreement for the polyester laminates can only be obtained when the values of α_t used are those for wet laminates. The large thermal strains previously reported for the polyester laminates can therefore be explained by small quantities of water in the matrix which are not readily removed during post-curing.

1. Introduction

The construction of a typical fibre-reinforced plastic composite involves curing and/or post-curing at elevated temperatures to obtain the optimum properties of the resin matrix. On cooling from this elevated temperature, thermal strains are developed within the composite. For a unidirectional laminate they are present at the micromechanics level because of the thermal expansion coefficient mismatch between fibre and matrix. For angle-ply laminates they are the result of the mismatch in properties between plies of different orientation. These thermal strains can have a major effect on the overall material performance of a cross-ply laminate. For example the residual thermal strains in an angle-ply laminate can approach values comparable to the failure strain of the transverse ply. At worst this can lead to failure of the ply and at best reduces the strain that may be applied to the laminate prior to transverse cracking. Transverse cracking in cross-ply laminates in which the fibres are at right angles has been studied extensively [1–4].

It has been shown [1] that on cooling from a temperature T_1 to a lower temperature T_2 the thermal strain in the transverse ply in the longitudinal direction of a $0°/90°/0°$ composite, ϵ_{tl}^{th}, is given by

$$\epsilon_{tl}^{th} = \frac{E_l b (\alpha_t - \alpha_l)(T_1 - T_2)}{(E_l b + E_t d)} \qquad (1)$$

where E_l and E_t are the Young's moduli of the undirectional plies parallel to the fibres (the longitudinal or $0°$ direction, l) and perpendicular to the fibres (the transverse or $90°$ direction, t), respectively. α_l and α_t are the linear expansion coefficients of the $0°$ and $90°$ plies. b and $2d$ are $0°$ and $90°$ ply thicknesses, respectively. T_1 is the temperature at which strain is first built into the laminate, and is dependent upon the viscoelastic nature of the matrix resin. T_2 is the temperature at which ϵ_{tl}^{th} is measured.

Using Equation 1, it is possible to calculate the value of ϵ_{tl}^{th} when all of the terms are known. In most cases the values of α_t, α_l and T_1 are not known and to overcome this problem, a method of determining thermal strain has been developed by Bailey *et al.* [1]. This consists of making an unbalanced cross-ply laminate with a $0°/90°$ configuration. Due to the mismatch in expansion coefficients of the two plies, cooling from post-cure temperature causes a thin beam sample to curve in the manner of a bimetal strip. Timoshenko [5] has shown that

$$(\alpha_t - \alpha_l)(T_1 - T_2) = \frac{(b + d)}{2\rho}$$
$$+ \frac{(E_l b^3 + E_t d^3)}{6\rho(b + d)}\left[\frac{1}{E_l b} + \frac{1}{E_t d}\right] \qquad (2)$$

where ρ is the radius of curvature of the beam.

Thus by measuring the value of ρ at some temperature T_2 and from known values of b, d, E_1 and E_t it is possible to calculate the whole term $(\alpha_t - \alpha_1)(T_1 - T_2)$ and hence ϵ_{tl}^{th}. This technique of determining the residual thermal strains is very simple, and takes into account any stress relaxations occurring during the cooling process, and eliminates the need for measurement of α_1, α_t and T_1 individually.

The thermal strains present in glass fibre-reinforced epoxy and polyester cross-ply laminates measured using the above technique have been reported [1, 3, 4]. These laminates were prepared using the same glass rovings but the thermal strains recorded were significantly different: typically 0.28 and 0.45% in the fully post-cured epoxy and polyester laminates, respectively. (The values reported earlier for the epoxy composites are less than 0.28% because the matrix had a lower softening point.) The difference in values cannot be explained by the resins freezing at different temperatures because the epoxy resin has a higher softening temperature than the polyester but developed less thermal strain. This suggested that the expansion coefficients of the two resins were different, a conclusion which has been confirmed experimentally in a previous paper [6].

In this paper we report values of thermal strain measured experimentally using unbalanced laminates and compare them with predicted values. The predicted values were calculated using Equation 1 from experimentally determined values of T_1 and expansion coefficients [6].

2. Experimental procedures
2.1. Materials
The thermosetting resins selected for this study were Crystic 272 (Scott Bader & Co. Ltd) and Epikote 828 (Shell Co. Ltd) since E-glass fibre-reinforced laminates incorporating these resins have been studied extensively [1–4, 6–8]. The glass fibres used in the laminates were Silenka 051 P 1200 tex E-glass fibres.

2.2. Production of unbalanced 0°/90° cross-ply laminates
The production of epoxy cross-ply laminates was accomplished by winding E-glass rovings onto metal frames to form the individual plies. These frames were then stacked in the required order to produce an unbalanced 0°/90° laminate. The fibres were then impregnated with the epoxy resin

using a high-temperature vacuum impregnation technique [7]. Because of the low viscosity of the hot resin, no problems of wetting out of the fibres were encountered and laminates with a volume fraction of 55% ± 5% were obtained reproducibly using this one stage technique.

Polyester cross-ply laminates were made using a two-stage process. The glass rovings were wound onto metal frames as before but a single ply was wetted out using the activated resin and allowed to cure for 24 h. Onto this a second ply was layed up with its fibres at right-angles to those in the gelled ply. This layer was allowed to gel for a further 24 h. This two-stage lamination procedure has been found to produce laminates substantially free of damage, which is in contrast to a one-stage procedure [3]. Laminates with a volume fraction of 34% ± 2% were produced, which is the result of the high viscosity of the polyester resin compared to the epoxy resin. Care was taken to remove resin during the wetting out procedure for the polyester laminates with higher volume fractions of glass fibres.

Post-curing of the beams was accomplished in an air circulating oven with temperature control to within ± 1° C.

2.3. Measurement of thermal strain and its temperature dependence
From the work of Bailey et al. it was known that in order to measure the thermal strain developed in a 0°/90°/0° laminate it was only necessary to measure the radius of curvature, ρ, of an unbalanced 0°/90° laminate with known values of b, and d [1]. Thus after post-curing for the required time the unbalanced beams were cooled to ambient temperature and placed on a flat steel plate where the maximum displacement, δ, was measured using a travelling microscope accurate to ± 0.01 mm (Fig. 1). At the same time the longitudinal and transverse ply thicknesses, b and d, were measured at 5 separate positions. The laminate thickness, h, ($h = b + d$), was also recorded at these positions using a micrometer as an independent check. The value of h and those of $(b + d)$ at any point were in good agreement to ± 0.05 mm. However the values of b and d were used for each individual laminate. The value of the chord length, $2x$, (see Fig. 1) was measured using a steel rule to an accuracy of ± 0.5 mm between the two points of contact. The radius of curvature, ρ, was then
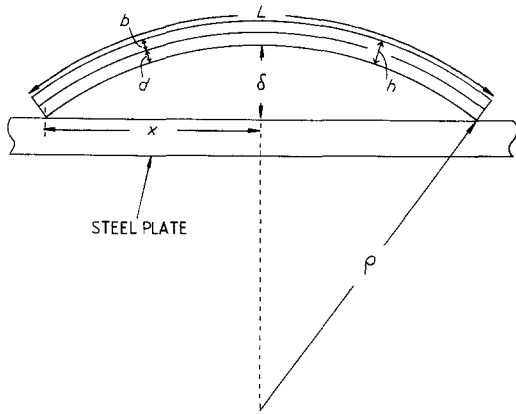
Figure 1 A model of an unbalanced 0°/90° cross-ply beam showing the geometric basis of the measurements of thermal strains. b, d are 0° and 90° ply thicknesses, respectively. L, x, δ, ρ are beam length, semi-chord length, beam displacement and radius of curvature, respectively.
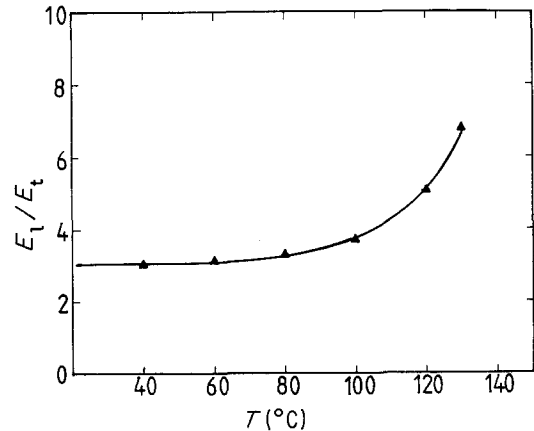

Figure 2 Variation of the ratio of longitudinal and transverse Young's moduli (E_l/E_t) with temperature T for a glass fibre-reinforced polyester laminate of volume fraction of fibres (V_f) of 0.35.

calculated from Equation 3 using the measured values of δ and x.

$$\rho = \frac{\delta^2 + x^2}{2\delta} \qquad (3)$$

Equation 3 can be obtained from simple trigonometrical considerations of Fig. 1.

Since it is implicit in the analysis of Timoshenko [5] that the bent beam takes up the shape of an arc of a circle, it was checked visually for congruence with a circle of radius ρ calculated from Equation 3. In all cases good agreement was found, even for samples with large thermal strains and hence small values of ρ.

Also implicit in the analysis is that the width of the beam, ω, is small relative to its length, L, so that any forces acting across the width are negligible, and do not affect the measured value of δ. As ω approaches L, the beam becomes a plate and on cooling a saddle-shape is expected. It has been observed that unsymmetrical laminate plates with thin plies adopt one or other of the two stable curved configurations [9]. The thicker cross-ply laminates used in this study, on the other hand, adopted the saddle-shape predicted by classical lamination theory. The effect of varying the beam width, ω, from 50 down to 5 mm (keeping the beam length, L, constant at 200 mm) on the measured value of δ and hence the calculated value of ρ was investigated. It was found that for values of ω less than 20 mm, i.e. when $\omega \leqslant 0.1 L$, δ was invariant. Normally, coupons

with $\omega \simeq 10$ mm were used as these were most conveniently prepared and used.

Examination of Equation 2 reveals the dependence of $(\alpha_t - \alpha_l)(T_2 - T_1)$ and hence ϵ_{tl}^{th}, on the ratio E_l/E_t. In the original analysis of Timoshenko [5] in which metal beams are considered, this ratio is normally in the range 0.5 to 2 and is considered insensitive to temperature changes. In the case of the composite beams considered here, however, the ratio E_l/E_t will be in the range 3 to 4 and dependent on the fibre volume fraction of the transverse and longitudinal plies. Of more importance is the fact that E_t, which is dominated by the properties of the matrix is expected to be more sensitive to temperature than E_l, so that the ratio E_l/E_t would vary. In order to investigate the order of any change in this ratio we have measured the dynamic modulus of the fully post-cured polyester resin using a Polymer Labs DMTA unit. Using this information we have calculated the values of E_l and E_t using the equation of Halpin and Tsai quoted by Ashton *et al.* [10] and have plotted the ratio (E_l/E_t) as a function of temperature (Fig. 2). This result suggests that the change in E_l/E_t below the glass transition temperature (T_g) of the resin is not large so that the use of Equation 2 is valid.

The technique of Bailey *et al.* although useful, only gave the total thermal strain at room temperature and did not allow the temperature dependence of ϵ_{tl}^{th} to be determined [1]. To overcome this problem the travelling microscope was used to follow the deflection, δ, of the beam as it was
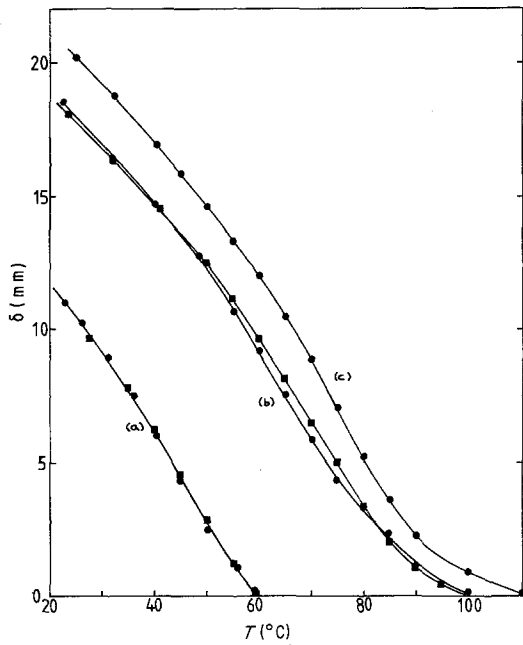
Figure 3 The temperature dependence of the beam displacement (δ in Fig. 1) for the polyester/glass fibre composites post-cured at different temperatures: (a) 50° C; (b) 130° C – slow cooled; (c) 130° C – fast cooled; ●, heating; ■, cooling of beam.

heated or cooled in a glass fronted oven. This results in a plot of beam deflection as a function of temperature, such as shown in Figs. 3 and 4. From such plots it was observed that for the polyester laminates post-cured at 130° C, (i.e.
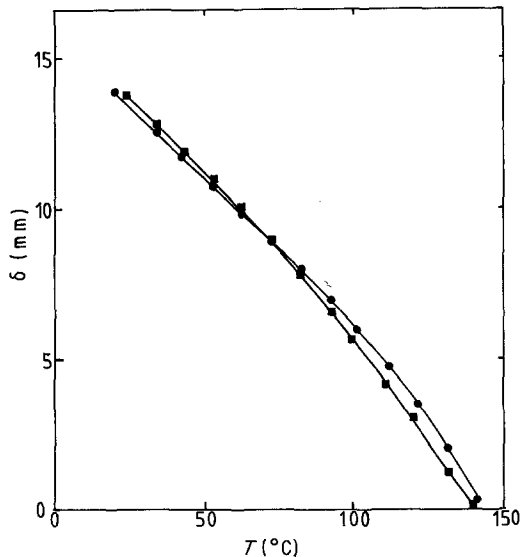

Figure 4 The temperature dependence of the beam displacement for (δ in Fig. 1) an epoxy/glass fibre composite post-cured at 150° C. ●, heating; ■, cooling.

above the maximum T_g of the resin [6]), the thermal strain which develops was cooling-rate dependent, thus fast cooling gives rise to a T_1 (the temperature at which thermal strain is first built into the laminate) of 110° C which induces a larger thermal strain than slow cooling, where T_1 is in the range 90 to 100° C. This effect accounts for the limited discrepancy between the reported thermal strains for polyester laminates post-cured at 130° C [3, 4]. Once this cooling-rate effect had been identified all specimens were slow cooled from the post-cure temperature. This was achieved by leaving the specimens to cool inside the oven after post-curing. The behaviour of an epoxy laminate post-cured at 150° C is shown in Fig. 4. For these laminates no measurable difference in T_1 or ϵ_{tl}^{th} was found on changing the cooling rate.

Since it was difficult to accurately measure the chord length, $2x$, at different temperatures in the oven a new method of calculating the radius of curvature, ρ, was required. Since the length of the beam, L, can be shown to be relatively insensitive to temperature change, the radius of curvature, ρ, can be calculated using the equation

$$\frac{1}{\rho} = \frac{2}{L} \cos^{-1}(1 - \delta/\rho) \qquad (4)$$

Note: the argument is in radians.

The calculation involved an iterative procedure which was found to converge rapidly. The value of L used in Equation 4 was calculated from the room temperature values of δ and x, measured on removal from the oven, using Equation 5 which is obtained from a simple trigonometric consideration of Fig. 1.

$$L = \frac{\pi}{360} \sin^{-1}\left[\frac{2\delta x}{\delta^2 x^2} \frac{(\delta^2 + x^2)}{2\delta}\right] \qquad (5)$$

Thus from the simple plots of δ against temperature it is possible using Equations 4 and 2 to calculate the term $(\alpha_t - \alpha_l)(T_1 - T_2)$ as a function of temperature. Such plots can be related directly to the thermal strain through Equation 1.

3. Results
The thermal strain which develops on cooling polyester laminates to room temperature from the post-cure temperature is shown in Fig. 5. These results, for two different volume fractions, were obtained by measuring the radius of curvature of unbalanced laminates at 23° C, as described in Section 2.3.
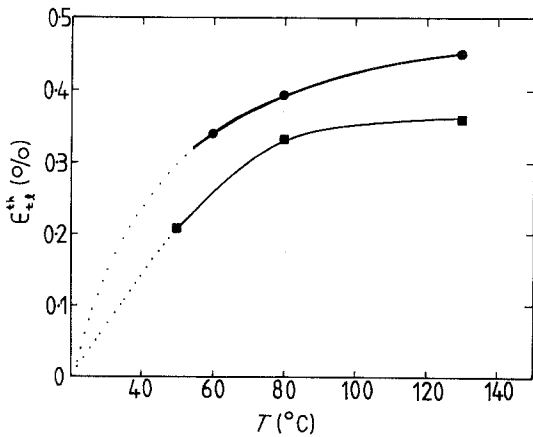
Figure 5 The magnitude of the measured thermal strains ϵ_{tl}^{th} in glass fibre-reinforced polyester resin (Crystic 272) at different fibre volume fractions (●, 0.33; ■, 0.52) and post-cure temperatures.

Fig. 6 shows the calculated variation of the room temperature longitudinal and transverse expansion coefficients of unidirectional polyester laminates as a function of fibre volume fraction. These curves were calculated from the equations of Schapery [11] using resin and fibre properties reported elsewhere [6] and given in the caption. The value of $(\alpha_t - \alpha_l)$, to which ϵ_{tl}^{th} is directly related, is shown as a dotted line.

It has been shown that Equation 1 relates the thermal strain to the difference in expansion coefficients, $(\alpha_t - \alpha_l)$, the temperature difference $(T_1 - T_2)$, and the ratio of the stiffness of the two plies, $[E_l b/(E_l b + E_t d)]$. Since, as shown in Fig. 2, the ratio E_l/E_t does not vary significantly
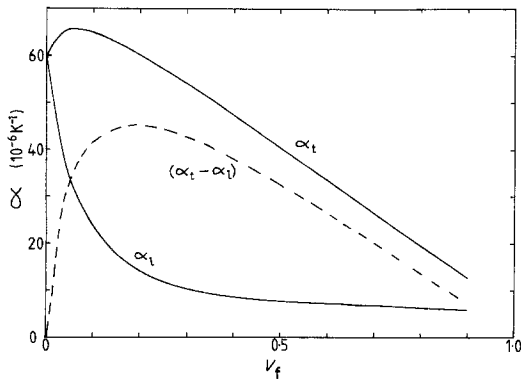

Figure 6 The theoretical variation of α_t, α_l and $(\alpha_t - \alpha_l)$ at $20°$ C with glass fibre volume fraction, V_f, using the Schapery equations [11]. $\alpha_m = 60 \times 10^{-6} K^{-1}$, $\alpha_f = 5 \times 10^{-6} K^{-1}$, $E_m = 4\,GPa$, $E_f = 72\,GPa$, $\nu_m = 0.4$, $\nu_f = 0.2$, E_l and ν_c have been calculated from the law of mixtures.
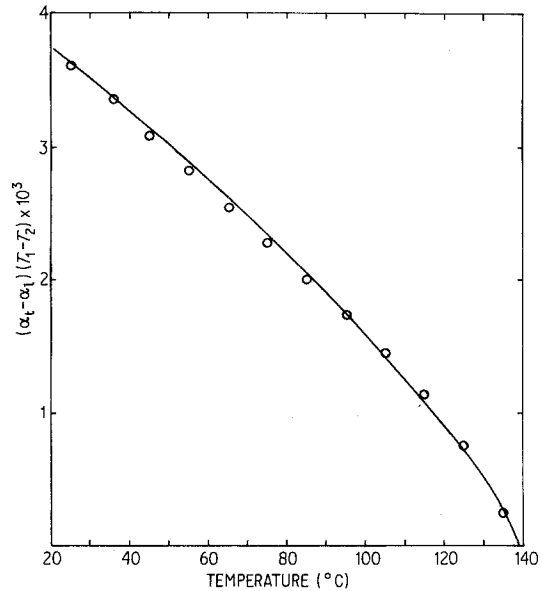

Figure 7 The measured values of $(\alpha_t - \alpha_l)(T_1 - T_2)$ for $150°$ C post-cured epoxy laminate obtained from $0°/90°$ beams (continuous line) and the circles are for those predicted from known values of α_t and α_l [6]. These values are directly proportional to the thermal strains (Equation 1).

over the temperature range up to $100°$ C the thermal strain at any temperature T_2 is related directly to the term $(\alpha_t - \alpha_l)(T_1 - T_2)$. Thus the experimentally determined δ/T curves for the fully post-cured, slowly cooled laminate have been converted into graphs of $(\alpha_t - \alpha_l)(T_1 - T_2)$ against T_2 using Equation 2 and are shown as the solid lines in Figs. 7 and 8. Also included in these figures are values of $(\alpha_t - \alpha_l)(T_1 - T_2)$ calculated from known values of α_t, α_l, and T_1 for each laminate. The values of α_t and α_l had been measured in a previous study [6], while the values of T_1 were obtained from Figs. 3 and 4.

4. Discussion

The values of ϵ_{tl}^{th} which develop in unbalanced polyester laminates after post-curing are shown in Fig. 5. As can be seen, increasing the post-cure temperature has increased the level of thermal strain. It is of note that post-curing at $130°$ C does not give rise to strains much larger than are present in specimens post-cured at $80°$ C. This is because the "effective glass transition temperature" of the slowly cooled laminate is in the range 90 to $100°$ C, thus post-curing at $130°$ C only increases the effective value $(T_1 - T_2)$ by 10 to $20°$ C. (Note, the "effective" T_g of the laminate is
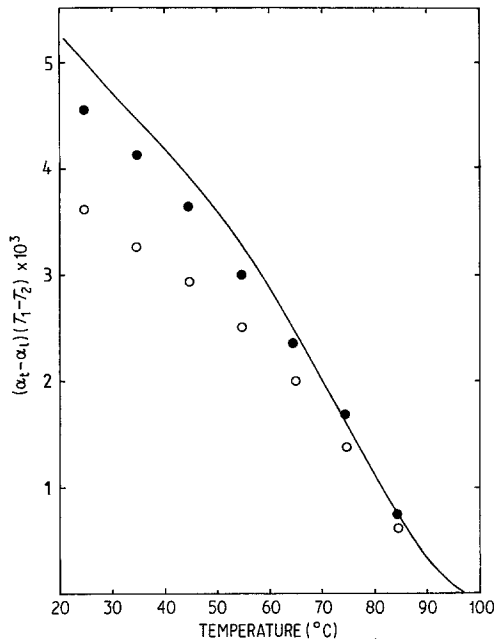
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Figure 8 The measured values of $(\alpha_t - \alpha_l)(T_1 - T_2)$ for fully post-cured (130° C) polyester laminate obtained from 0°/90° beams (continuous line) and those predicted from known values of α_t and α_l [6]. Dry laminates (○), wet laminates containing 0.15% water after 2 days immersion (●). These values are directly proportional to the thermal strains.

defined as the temperature at which the unbalanced beam ceases to be flat and corresponds to the temperature at which strain first starts to build into the laminate, i.e. T_1). As expected, increasing the glass fibre volume fraction leads to a decrease in the measured thermal strain. This is because at a given post-cure temperature the value of $(T_1 - T_2)$ is fixed relative to room temperature, whereas the term $(\alpha_t - \alpha_l)$, on which ϵ_{tl}^{th} is also dependent, decreases with increasing fibre volume fraction. In fact, Fig. 6 shows that $(\alpha_t - \alpha_l)$ exhibits a maximum in the range of $V_f = 0.1$ to 0.2, but this is below that of the experimental laminates.

The deflection behaviour of unbalanced polyester laminates, Fig. 3, shows several points of interest. Firstly, increasing the post-cure temperature increases the glass transition temperature of the resin and hence T_1 of the laminate. This is consistent with the previously observed expansion behaviour of the resin [6]. Secondly, the effect of the cooling rate on the value of T_1 and hence ϵ_{tl}^{th} is consistent with a viscoelastic resin system in which T_1 is cooling-rate dependent. Thus fast cooling allows less time for molecular arrange-

ment so that more free volume is frozen into the molecular structure. Slow cooling allows a situation closer to equilibrium to be attained with a lower T_g. What is of possible industrial interest is that slow cooling from the above maximum glass transition temperature introduces approximately 10% less thermal strain at room temperature than fast cooling from the same temperature. That the epoxy laminate post-cured at 150° C, Fig. 4, did not show a measurable change in T_1 with cooling rate is a reflection of the different structure of the epoxy resin.

Fig. 7 shows the $(\alpha_t - \alpha_l)(T_1 - T_2)/T_2$ curve computed from the experimentally determined displacements of the unbalanced epoxy laminate. Also included are values of $(\alpha_t - \alpha_l)(T_1 - T_2)$ computed from experimentally determined values of α_t and α_l [6] using the value of T_1 shown in Fig. 4. There is good agreement between the computed and experimental values showing that the level of thermal strain can be readily predicted from this analysis using the known expansion characteristics of the individual plies.

The above result supports the validity of the analysis and enables the behaviour of the polyester laminate to be interpreted with more confidence since the computed and experimental values of $(\alpha_t - \alpha_l)(T_1 - T_2)$ are not in such good agreement. The results are shown in Fig. 8 where it can be seen that experimental values are larger than predicted from the measured values of α_t and α_l of the individual plies.

Since it was known [6] that $(\alpha_t - \alpha_l)$ for such polyester laminates increases with small amounts of absorbed water a second set of $(\alpha_t - \alpha_l)(T_1 - T_2)$ values were calculated using values of expansion obtained from a laminate sample immersed in water for 2 days. These values are shown as filled circles in Fig. 8 and much better agreement between experimental and predicted values is observed. Since the increase in $(\alpha_t - \alpha_l)$ was associated with only 0.15 wt % water it suggests that the anomalously high thermal strains in these polyester laminates can be explained by the presence of a small quantity of water present in the matrix. Thus retained moisture in a polyester laminate after post-curing gives rise to a larger thermal strain on cooling to room temperature than would be produced if the laminate were "dry". As yet, we have not determined the nature of the water in the composite. Since it is not to be removed from a 0°/90° beam during

post-curing at 130° C for 1.5 h, it is probably strongly bound to the resin. An increase in the expansion coefficient of an epoxy resin and its composites due to absorbed water has been reported previously [12]. The epoxy resin used in this study was also found to absorb water but the effect on the expansion coefficient was only measurable after several weeks immersion. What is of interest here is the apparent sensitivity of the polyester resin to small quantities of absorbed water.

In a previous paper [6] we discussed the evidence for the idea that the polyester resin used in this study has a microstructure consisting of densely cross-linked particles in a less densely cross-linked matrix. We postulated that the sensitivity of the polyester resin to small quantities of water was due to either the rapid diffusion of water into or a more efficient plasticization of the less densely cross-linked regions. The effect that this has on the thermal strains generated in such laminates has been demonstrated.

As a contrasting effect the ingress of water into a post-cured unbalanced laminate at room temperature causes a reduction of the strain in the laminate. This is because as the water is absorbed the transverse ply swells at a greater rate in the axial direction than the longitudinal ply. From a practical view-point this can be an advantage in that the laminate contains less strains but against this must be balanced the lower T_g and increased temperature sensitivity of a wet laminate. It should be emphasized that if such a laminate is then subjected to a thermal cycle, this could lead to higher thermal strains than were present initially.

5. Conclusions
The thermal strains present in polyester cross-ply composites have been measured experimentally from the deflection of an unbalanced laminate and compared with values predicted from the measured expansion coefficients of the individual plies. It is found that agreement can only be obtained when the chosen values of expansion coefficients are those for a wet laminate.

Good agreement between experimental and calculated values of thermal strain are observed in the epoxy resin based laminates.

References
1. J. E. BAILEY, P. T. CURTIS and A. PARVIZI, *Proc. Roy. Soc. London* **A366** (1979) 599.
2. J. E. BAILEY and A. PARVIZI, *J. Mater. Sci.* **13** (1978) 2131.
3. F. R. JONES, A. R. WHEATLEY and J. E. BAILEY, "Composite Structures", edited by I. H. Marshall (Applied Science Publishers, Barking, 1981) p. 415.
4. 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.
5. S. TIMOSHENKO, *J. Opt. Soc. Amer.* **11** (1925) 233.
6. F. R. JONES, M. MULHERON and J. E. BAILEY, *J. Mater. Sci.* **18** (1983) 1522.
7. F. R. JONES, J. W. ROCK and J. E. BAILEY, *ibid.* **18** (1983) 1059.
8. J. E. BAILEY and A. PARVIZI, *ibid.* **16** (1981) 649.
9. M. W. HEYER, *J. Comp. Mater.* **15** (1981) 175.
10. J. E. ASHTON, J. E. HALPIN and P. H. PETIT, "Primer on Composite Materials: Analysis" (Technomic, Stamford, 1969).
11. R. A. SCHAPERY, *J. Comp. Mater.* **2** (1968) 380.
12. R. De IASI and J. B. WHITESIDE, "Advanced Composite Materials — Environmental Effects", edited by J. R. Vinson (ASTM-STP 658, Philadelphia, 1968) p. 2.