

Thermal expansion characteristics of PEEK composites

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The thermal expansion behaviour of several fibre-reinforced PEEK composites is assessed. It is shown that thermal expansion behaviour is consistent, and changes in a predictable manner with changes in fibre type. Using a composite manufactured such that no interfacial bonding took place, it is demonstrated that compressive forces caused by differential thermal contraction of fibre and matrix are sufficiently large to dominate behaviour in a direction parallel to the fibres. This suggests that PEEK composites should be resistant to changes in thermal expansion behaviour with repeated thermal cycling, and such resistance is demonstrated for AS4/PEEK (APC-2/AS4). It is shown that conventional models for predicting laminate response from unidirectional composite properties are valid for such materials, but it is also shown that the common analytical models for calculating transverse fibre behaviour from composite properties are inaccurate.

1. Introduction

The thermal expansion behaviour of continuous-fibre-reinforced polymeric composite materials was extensively characterized in the late 1960s and early 1970s. Those studies focused exclusively on the first generation of brittle matrix materials. Today there is a new generation of thermoplastic matrix composites which have dramatically different characteristics in respect of toughness, and may be expected to be subtly different in their thermal expansion behaviour. For example, the designed strong interface and inherent resistance to microcracking in some of these materials may improve the resistance to thermal cycling-induced changes in properties. Tough thermoplastics such as poly-aryl-ether-ether-ketone (PEEK) are typically reinforced with carbon or graphite fibres, which have a negative coefficient of thermal expansion (CTE) along their length. Hence we have a polymeric phase, which has a high, positive CTE, and a stiff reinforcement which exert forces in opposite directions as the temperature changes.

Calculation of CTE values for unidirectionally reinforced materials is difficult due to the fact that the expansion behaviour of the fibres is always inferred from composite properties: hence we can never obtain an independent assessment. Measurement of behaviour in such materials is also difficult because of the small dimensional changes involved, requiring the use of highly specialized and relatively uncommon apparatus.

The data presented here are the results of combined projects at the University of Salford and at ICI

Wilton. Work at the University of Salford was concentrated on the measurement of behaviour parallel to the fibre direction in unidirectional samples over the temperature range 83–393 K: ICI work addressed the behaviour of unidirectional composites in directions away from that of the reinforcement, and also the response of cross-ply laminates.

2. Theory

The linear coefficient of thermal expansion (CTE) of a fibre reinforced composite is controlled by the behaviour of the individual constituents. Parallel to the reinforcement direction in a unidirectional composite, it is the fibre which dominates behaviour due to the stiffness differential between fibre and matrix. The behaviour of materials in this direction can be modelled using a simple stiffness-modified rule of mixtures equation of the form [1]

$$\alpha_{11}^c = \frac{\alpha_{11}^f E_{11}^f V_f + \alpha_m E_m V_m}{V_f E_{11}^f + V_m E_m} \quad (1)$$

where α is the CTE, E is Young's modulus, V is the volume fraction, m denotes matrix, f denotes fibre, and 11 denotes the direction parallel to the fibres. Equation 1 was obtained for isotropic constituents having equal Poisson's ratios. Schapery [2] showed that the relationship also gives a good approximation of thermal expansion when the Poisson's ratios of the constituents differ.

Behaviour transverse to the fibre direction is more difficult to predict from basic constituent per-

formance, a factor which is usually attributed to changes in phase geometry and distribution in the radial direction. Chamberlain [3] produced a rather complex relationship based on consideration of each fibre as being surrounded by matrix in the form of a thick-walled cylinder

$$\alpha_2^c = \alpha_m + \frac{2(\alpha_2^f - \alpha_m)V_f}{v_m(F - V_f) + (F + V_f) + (E_m/E_f)(1 - v_{12}^f)(F - V_f)} \quad (2)$$

where F represents the packing fraction of the fibres, equal to 0.9609 for hexagonal close packing, and 0.7854 for square packing, and v is Poisson's ratio. In a rather neater analysis, Shapery [2] obtained, for an upper bound value, the relationship

$$\alpha_2^c = (1 + v_m)\alpha_m V_m + (1 + v_f)\alpha_f V_f - \alpha_{11}^c(v_f V_f + v_m V_m) \quad (3)$$

in which the behaviour of the composite parallel to the fibres is also included. The Schapery relationship is applicable to the case of isotropic components in an orthotropic composite, though other workers have argued that the expression is not self-consistent and requires the addition of a second fibre term to allow extension to fibre anisotropy thus [4]

$$\alpha_2^c = (1 + v_m)\alpha_m V_m \alpha_{2f} V_f + \alpha_{1f} v_{12}^f V_f - \alpha_{11}^c(v_f V_f + v_m V_m) \quad (4)$$

which was shown to give accurate results for Kevlar/epoxy composites. The relationships above give reasonable approximations for the behaviour of unidirectional materials in the principal orientation directions. The CTE at any angle θ to the fibre direction in a unidirectional composite has been shown by Pirgou *et al.* [5] to be given by

$$\alpha_\theta = \alpha_1^c \cos^2 \theta + \alpha_2^c \sin^2 \theta \quad (5)$$

which has been verified by a number of workers [6].

Calculation of the behaviour of bidirectional laminates of the form $(\pm \theta)$ is rather more complex, requiring the use of classical laminate theory. For a full exposition the reader is referred to Ashton *et al.* [7]. The calculations included in this report were carried out using the ICI laminate analysis program "COMLAN".

Through-thickness coefficients of thermal expansion are also briefly assessed in this study, because this is the one thermal expansion parameter which is almost universally ignored in similar work. The common perception that through-thickness CTE is the same for all laminates made using the same material is actually seriously flawed: this should be far from the case, because the assumption of similarity fails to take into account the Poisson's effect of the in-plane strains in each ply. It is possible to develop an expression for the through-thickness CTE which allows for the in-plane strains thus [8]

$$\alpha_3 = \frac{I_3 \sin^2 2\theta}{I_1 \cos^2 2\theta + I_2 \sin^2 2\theta} + \alpha_2 \quad (6)$$

$$\text{where } I_1 = E_{11} E_{22} \quad (7)$$

$$I_2 = G_{12} [E_{11} + E_{22}(1 + 2v_{12})] \quad (8)$$

$$I_3 = E_{11} G_{12} (\alpha_2 - \alpha_1)(v_{23} - v_{21}) \quad (9)$$

and θ is the interply angle. Further, there is likely to be a slight variation in coefficients of thermal expansion transverse to the fibres in the in-plane and out-of-plane directions due to changes in fibre/resin dis-

tribution. In most composite materials there is a thin resin-rich layer between neighbouring plies, which is necessary for interply bonding. The change in behaviour induced by this inhomogeneity is typically smaller than that due to laminate restraints described above, but the effect is nonetheless measurable in thermo-plastic composites.

3. Materials

A number of continuous-fibre-reinforced thermo-plastic composites were manufactured by ICI using a proprietary impregnation process. In all cases the matrix used was poly(aryl-ether-ether-ketone) (PEEK), and the fibre types examined are shown in Table I. Three of the fibres are carbon, derived from polyacrylonitrile (PAN): Hercules AS4, a similar experimental fibre and Hercules IM7. The AS4 and IM7 reinforced materials are commercially available composites, designated APC-2/AS4 and APC-2/IM7, respectively. The AS4 and experimental fibres are essentially identical, but the experimental type can be used to produce a composite in which no interfacial bonding is present. Types P75 and P100 are graphitic fibres produced by Amoco using a different precursor, mesophase pitch. Such fibres are significantly stiffer than the PAN types, but are extremely brittle. Finally, S-2 glass fibres are far less stiff than the graphite or carbon, and possess a positive CTE.

In each case standard processing conditions [9] were followed to allow production of 3 mm thick unidirectional samples and 2 mm thick angle-ply laminates for examination. Specimens approximately 3 mm wide and 15 mm long were cut from the centre of each laminate and prepared for testing. In the case of materials tested at Salford University this involved grinding the end faces of each rod to a slight dome shape, whilst the ICI-tested specimens were ground to ensure that the end-faces were parallel. Through-thickness CTE measurements were carried out on the laminates described above, using samples 2 and 3 mm thick.

TABLE I Composite reinforcements

Fibre type	Fibre tensile modulus (GPa)	Fibre volume fraction (%)
S2-Glass	76	62
Hercules AS4	234	62
Experimental	234	62
Hercules IM7	303	62
Thornel P75	524	55
Thornel P100	724	45

4. Experimental details

The absolute values of linear coefficient of thermal expansion parallel to the fibre direction in carbon fibre-reinforced composites of the types examined is extremely low, and in consequence, sensitive methods are required for their accurate determination. In this study a Fizeau interferometer at the University of Salford was used for measurements in this direction. The principal benefits of this method are two-fold; firstly, it provides a direct measurement of the linear CTE of the material under examination without recourse to a comparative standard, and is therefore free from the problems of calibration; and secondly very small changes in dimension (of the order of 3 nm, [5]) can be resolved.

The apparatus used in this part of the work has been described in detail elsewhere [10], and hence only brief details are given here. Two separate Fizeau interferometers were employed, covering the temperature ranges 83–296 K and 296–393 K, respectively. The equipment consists of an optical system with associated support structure of temperature monitoring and control, and vacuum equipment. In each case three of the columnar samples previously described were placed in position in a supporting ring, and used to separate the two optical flats of an interferometer such that a relative inclination between the flats of around 10^{-5} rad was produced. Fizeau fringes were thus produced in the wedge by the interference of light rays reflected from the aluminized upper surface of the bottom flat and the lower surface of the top flat. Collimated monochromatic light from a helium neon laser was used as the light source, and low-pressure helium was bled through the equipment during measurement. In all cases, low-temperature runs were carried out prior to heating above room temperature, and at least 45 min was allowed for the apparatus and specimens to stabilize at each temperature before readings were taken. To determine specimen expansion, the fringe position relative to a temperature invariant reference mark was determined, and therefore any change in specimen length could be determined. A schematic representation of the equipment is shown in Fig. 1.

Determination of CTE for directions away from that parallel to the fibres was carried out on a Perkin-Elmer TMA push-rod dilatometer apparatus using a

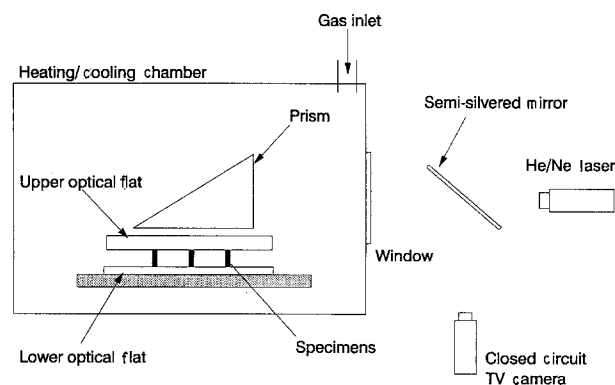


Figure 1 Schematic illustration of the laser interferometric measuring equipment.

heating rate of $5^{\circ}\text{C min}^{-1}$. Sample cooling was carried out by means of liquid nitrogen, and data were gathered over the total range 223–573 K. Owing to the fact that the dilatometric apparatus relies on transient heating, it is difficult to quote precise accuracy limits on the equipment. However, the absolute resolution of the dilatometer is approximately $0.5\ \mu\text{m}$, and hence for measurements transverse to the fibre direction in composites examined in this study an accuracy of $\pm 2.5\%$ is assumed in all cases.

A number of unidirectional specimens was thermally cycled over the range 113–393 K by Composite Optics Inc., San Diego, in order to test the effects of thermal fatigue on the material. Sets of AS4/PEEK composite were subject to 10 and 100 cycles over this range.

5. Results

For ease of analysis the coefficients of thermal expansion of the samples tested are shown in Tables II–V; in order to facilitate discussion of the results, primary data are presented in Figs 2–7.

5.1. Unidirectional samples

The change in linear coefficient of thermal expansion of composites measured in the direction parallel to the fibres are shown in Figs 2–7: although best fit polynomials to the raw data were calculated, these are not plotted. The form of the curves is quite complex, and it was found that a single polynomial expressions could not be found which expressed relationships between thermal expansion coefficient and temperature adequately for the carbon fibre-reinforced samples. However, best fit expressions between the temperature limits 80 and 300 K are noted under each curve. Figs 2–6 represent the behaviour of PEEK composites reinforced with graphitic fibres, whilst Fig. 7 shows the change in CTE of glass/PEEK with temperature. The expansion of the graphite fibre-reinforced materials is largely similar and self-consistent, with increasing fibre modulus leading generally to decreasing CTE values. In all cases except that for the glass-reinforced material the curves follow a characteristic U-shape, with the data from each successive experimental run being coincident. However, note that in all cases the first excursion to high temperature (i.e. above 370 K) resulted in a slightly lower CTE value than succeeding experiments. This effect was found to be more pronounced in off-axis measurements, and will be discussed more completely later. Unlike graphitic fibres, glass fibres have a positive CTE, and therefore the behaviour of their composites may be expected to differ significantly from PAN-based or pitch-based carbon fibre-reinforced materials.

Values of CTE for each sample at 296 K were calculated by fitting polynomials to the raw data and solving to find an instantaneous result; data are shown in Table II. The values shown can only be approximate due to the degree of scatter; upper and lower 95% confidence limits on the data are also shown.

Using the push-rod dilatometric equipment at ICI

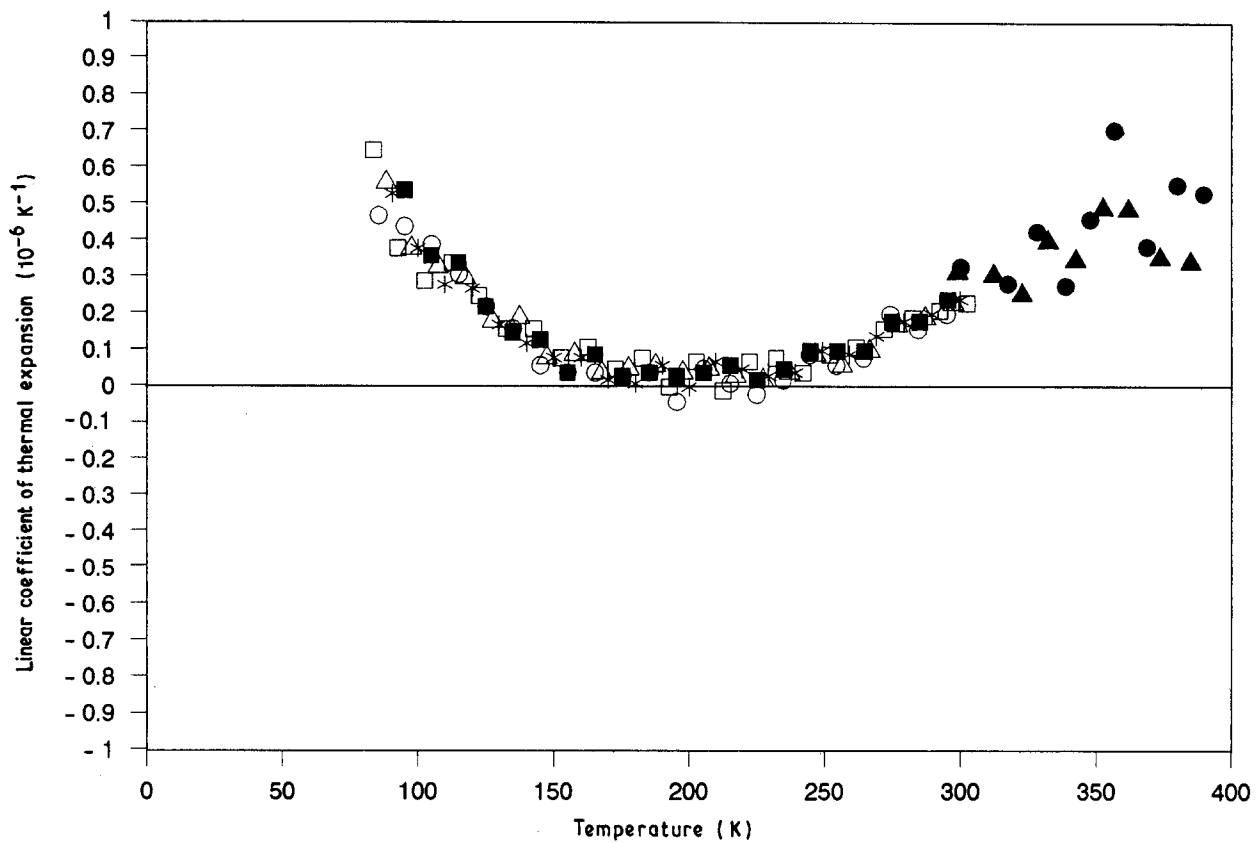


Figure 2 Change in linear CTE parallel to the fibre direction, AS4/PEEK. Best fit curve, 80–300 K: $\alpha = (3.15 \times 10^{-5} T^2 - 0.0132T + 1.3921) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (\square) 1, (\triangle) 2, (\circ) 3, ($*$) 4, (\blacksquare) 5; high-temperature runs: (\blacktriangle) 1, (\bullet) 2.

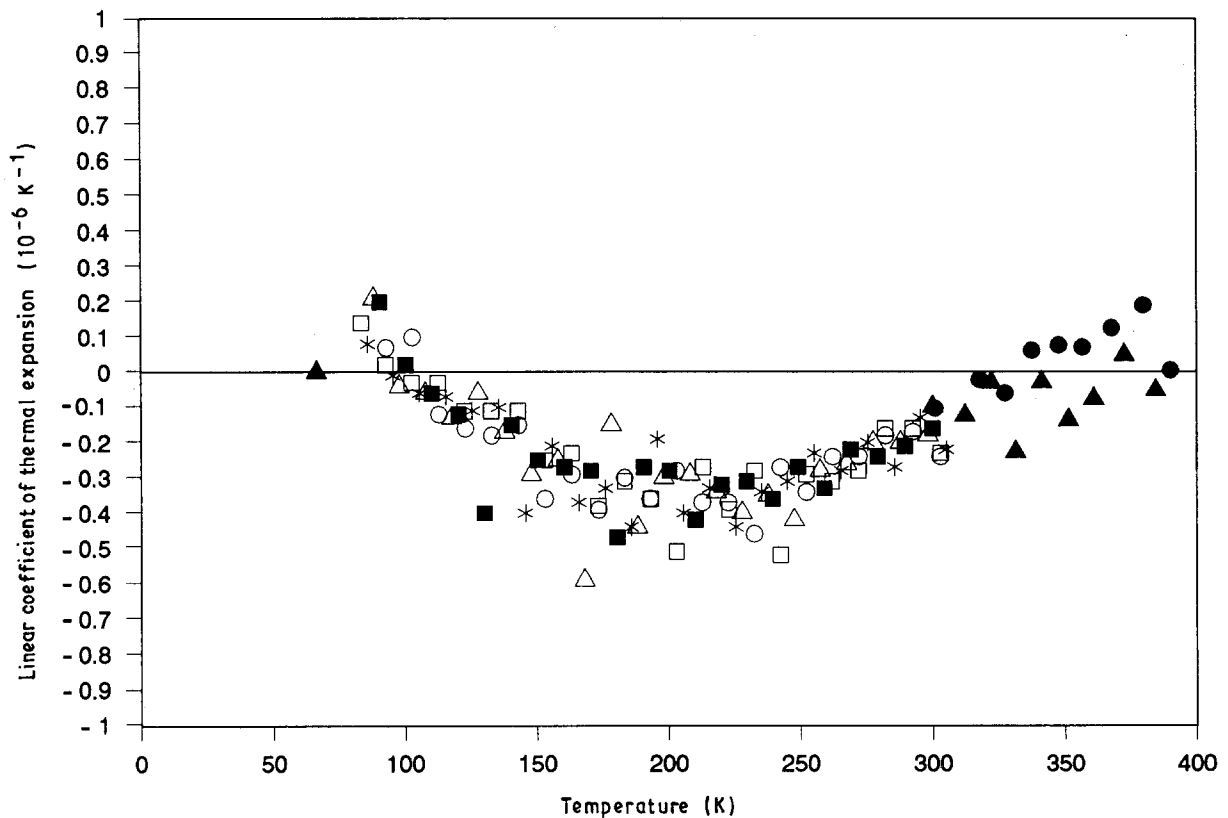


Figure 3 Change in linear CTE parallel to the fibre direction, IM7/PEEK. Best fit curve, 80–300 K: $\alpha = (2.83 \times 10^{-5} T^2 - 0.0121T + 0.935) \times 10^{-6} \text{ K}^{-1}$. For key, see Fig. 2.

Wilton, a number of unidirectional composites were examined in directions away from that of the reinforcement. A typical CTE/temperature plot is shown in Fig. 8, which illustrates the behaviour of an

AS4/PEEK laminate at 90° to the fibre direction. The absolute value of CTE undergoes little change until the glass transition of the polymer is approached, which suggests that the influence of the reinforcement

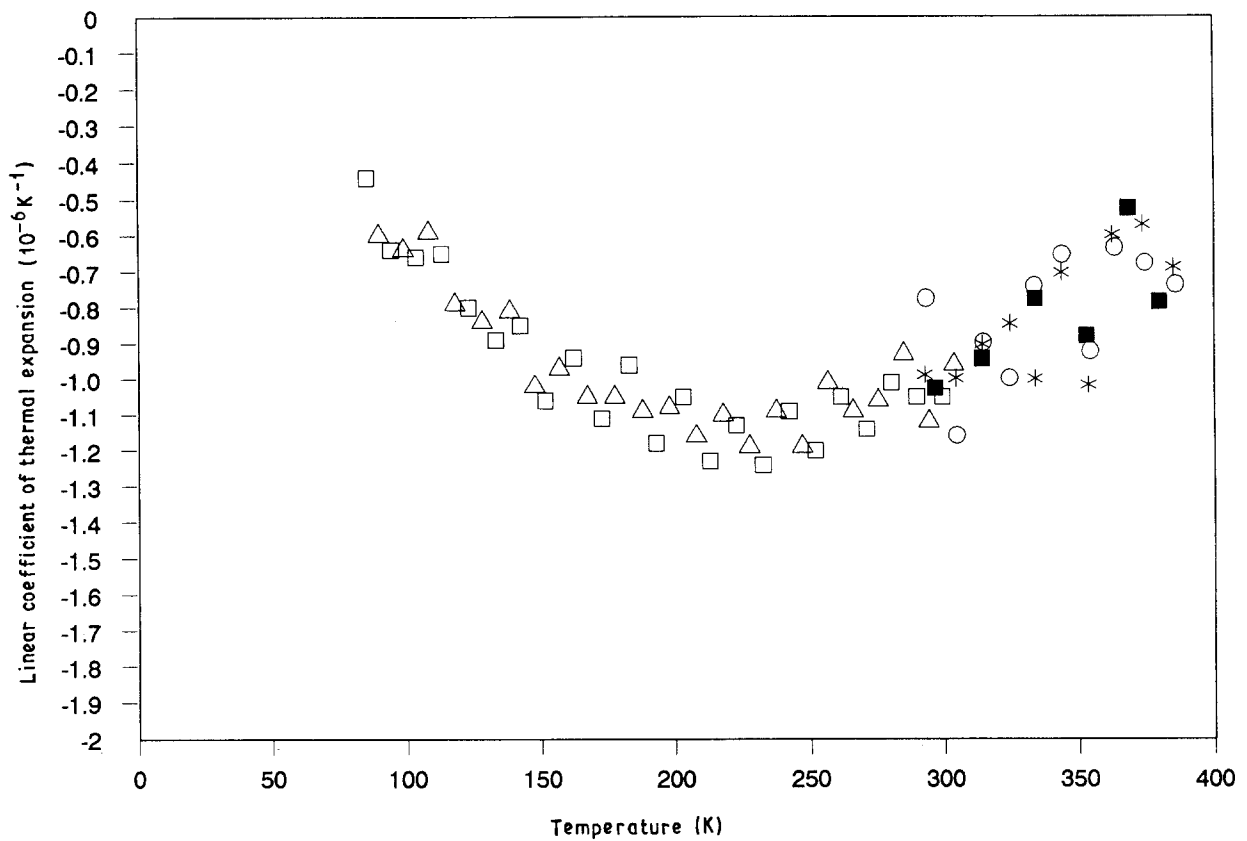


Figure 4 Change in linear CTE parallel to the fibre direction, P75/PEEK. Best fit curve, 80–300 K: $\alpha = (3.08 \times 10^{-5} T^2 - 0.01414T + 0.481) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (□) 1, (△) 2; high-temperature runs: (○) 1, (*) 2, (■) 3.

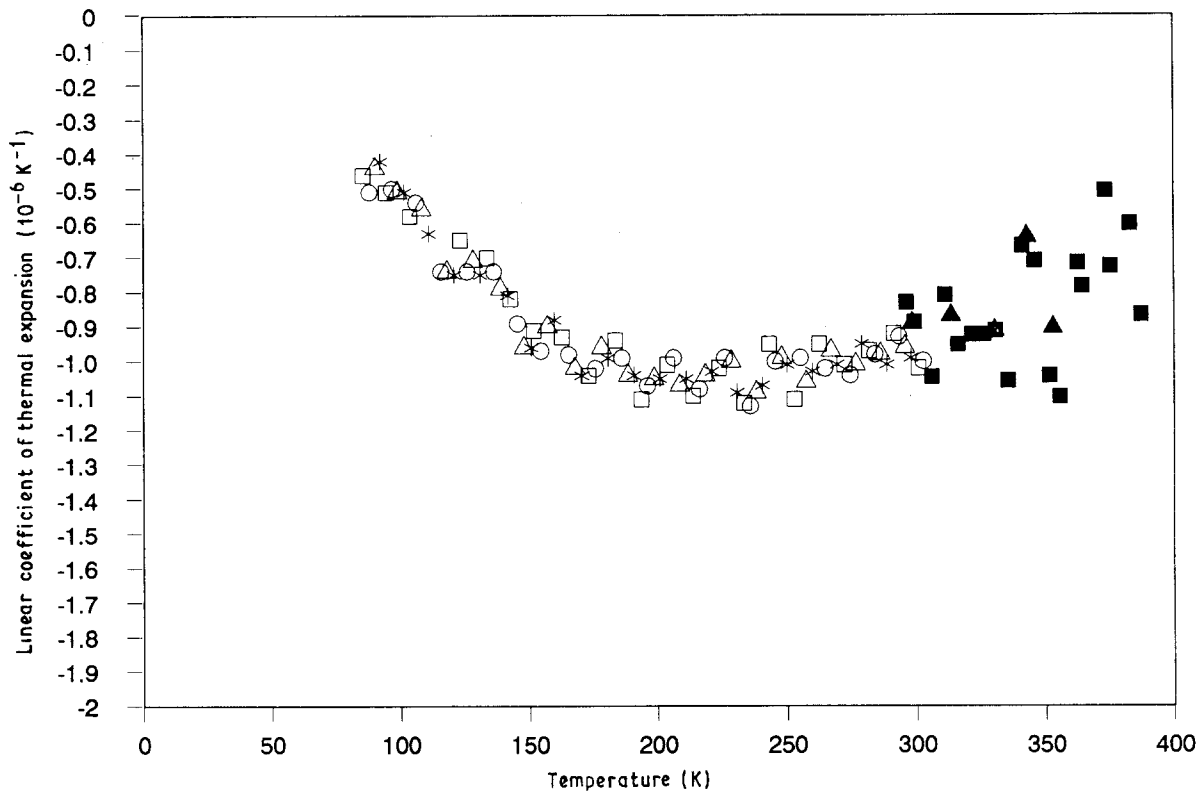


Figure 5 Change in linear CTE parallel to the fibre direction, P100/PEEK. Best fit curve, 80–300 K: $\alpha = (2.91 \times 10^{-5} T^2 - 0.01343T + 0.481) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (□) 1, (△) 2, (○) 3, (*) 4; high-temperature runs: (■) 1, (▲) 2.

is less in such laminates. Interestingly, an identical sample examined using the interferometric method displayed a large reduction in CTE on its first high-temperature excursion, as may be seen in Fig. 9.

Because this effect was absent in all of the dilatometer-examined specimens, the phenomenon has been attributed to an artifact of the test method. In the case of the interferometric results, each sample was held at

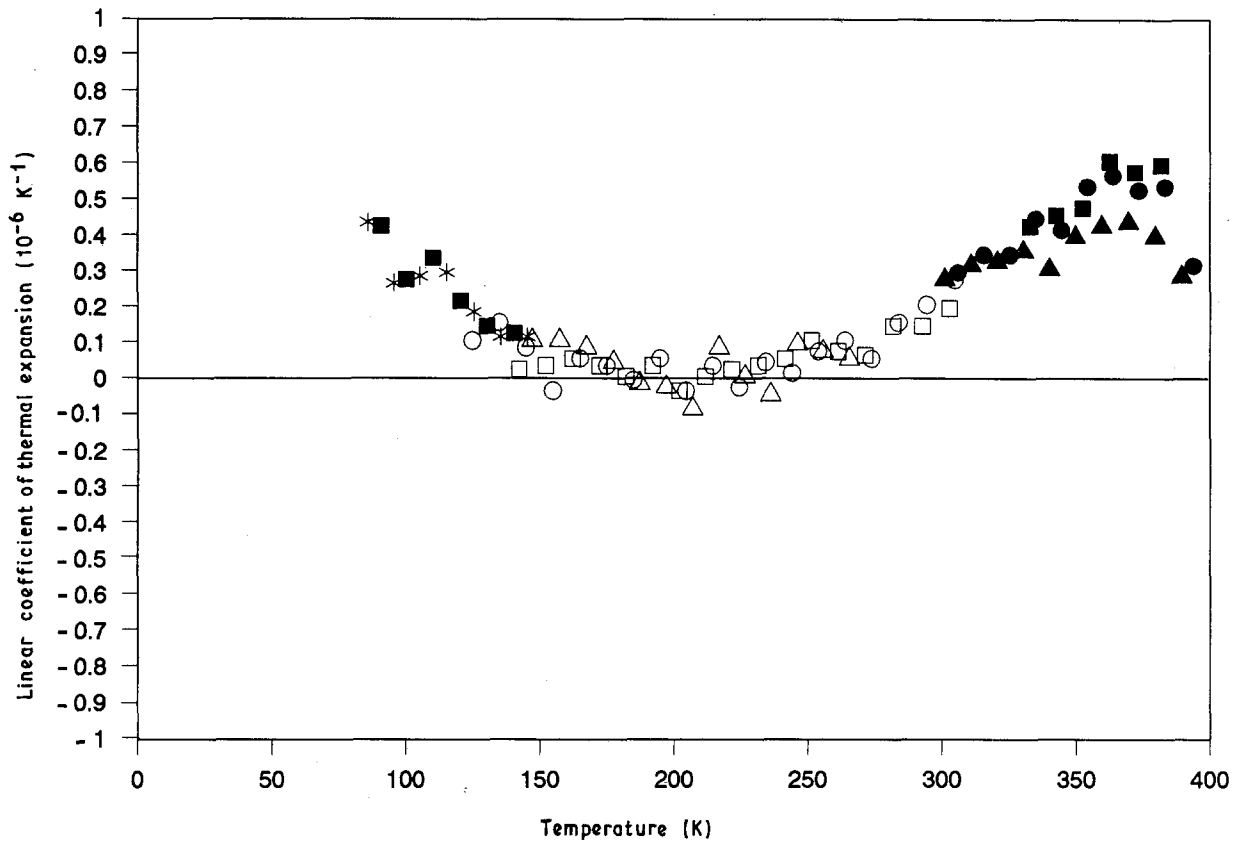


Figure 6 Change in linear CTE parallel to the fibre direction, experimental fibre/PEEK. Best fit curve, 80–300 K: $\alpha = (3.26 \times 10^{-5} T^2 - 0.0138T + 1.446) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (\square) 1, (\triangle) 2, (\circ) 3, (*) 4, (\blacksquare) 5; high-temperature runs: (\blacktriangle) 1, (\bullet) 2, (\blacksquare) 3.

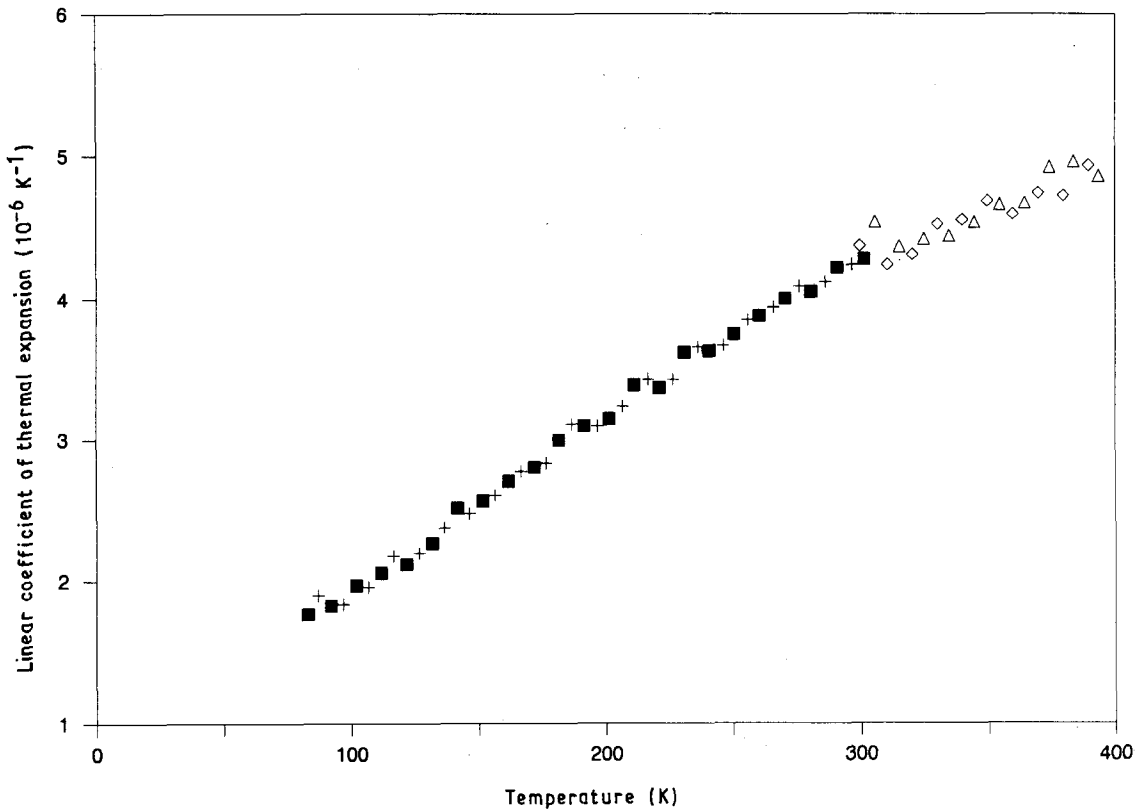


Figure 7 Change in linear CTE parallel to the fibre direction, S2 glass/PEEK. Best fit curve, 80–400 K: $\alpha = (-1.41 \times 10^{-5} T^2 + 0.01721T + 0.3174) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (\blacksquare) 1, (+) 2; high-temperature runs: (\diamond) 3, (\triangle) 4.

high temperatures for several hours during thermal stabilization; holding at temperatures just below the T_g results in the process of free-volume annealing, where the free volume associated with ends of mole-

cules in the polymer is reduced. This has been shown to cause matrix densification and therefore apparent shrinkage [11]. Prolonged high-temperature soaking of material in the dilatometric apparatus reproduced

TABLE II CTE parallel to the fibre direction at 296 K, calculated from best-fit curves through data. 95% confidence limits shown in parentheses

Reinforcement	Linear CTE ($\times 10^{-6} \text{ K}^{-1}$) at 296 K
S2-Glass	4.18 (+ 0.136, - 0.190)
Hercules AS4	0.24 (+ 0.090, - 0.078)
Experimental	0.24 (+ 0.094, - 0.097)
Hercules IM7	- 0.17 (+ 0.148, - 0.177)
Thornel P75	- 1.01 (+ 0.146, - 0.167)
Thornel P100	- 0.94 (+ 0.162, - 0.119)
Hercules AS4, 10 thermal cycles	0.27 (+ 0.110, - 0.064)
Hercules AS4, 100 thermal cycles	0.25 (+ 0.089, - 0.100)

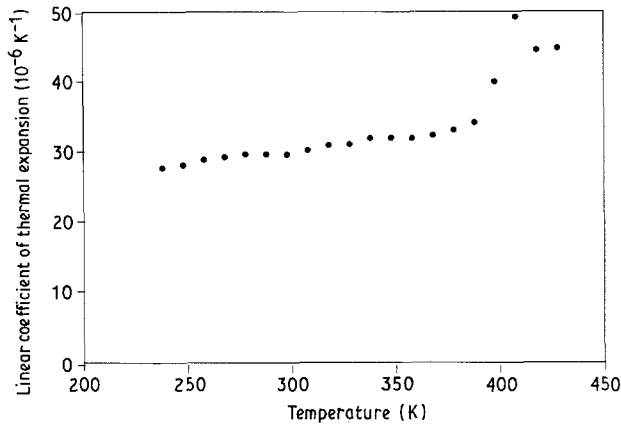


Figure 8 Change in linear CTE at 90° to the fibre direction, AS4/PEEK.

the effect, which serves to underline one of the primary differences between the two techniques: commercial dilatometry relies on non-equilibrated thermal fields during measurement, whilst the interferometric research tool allows true equilibrium to occur.

A summary of the off-axis measurements for each of the composites examined is shown in Tables III and IV: the predictability of behaviour is such that graphical presentation of raw data is unnecessary.

5.2. Angle-ply samples

A series of laminates of the form $[\pm \theta]_{4S}$ were produced using AS4/PEEK composite in order to test that classical laminate theory may be used to predict the thermal expansion behaviour of the material. In all cases the coefficient of thermal expansion showed a slight increase over the temperature range examined, within the limits of accuracy of the push-rod dilatometric equipment. A summary of the instantaneous data collected at 296 K is shown in Table V.

TABLE III CTE transverse to the fibre direction at 296 K

Reinforcement	Linear CTE ($\times 10^{-6} \text{ K}^{-1}$) at 296 K
S2-Glass	19.50
Hercules AS4	30.19
Hercules IM7	30.10
Thornel P75	30.60

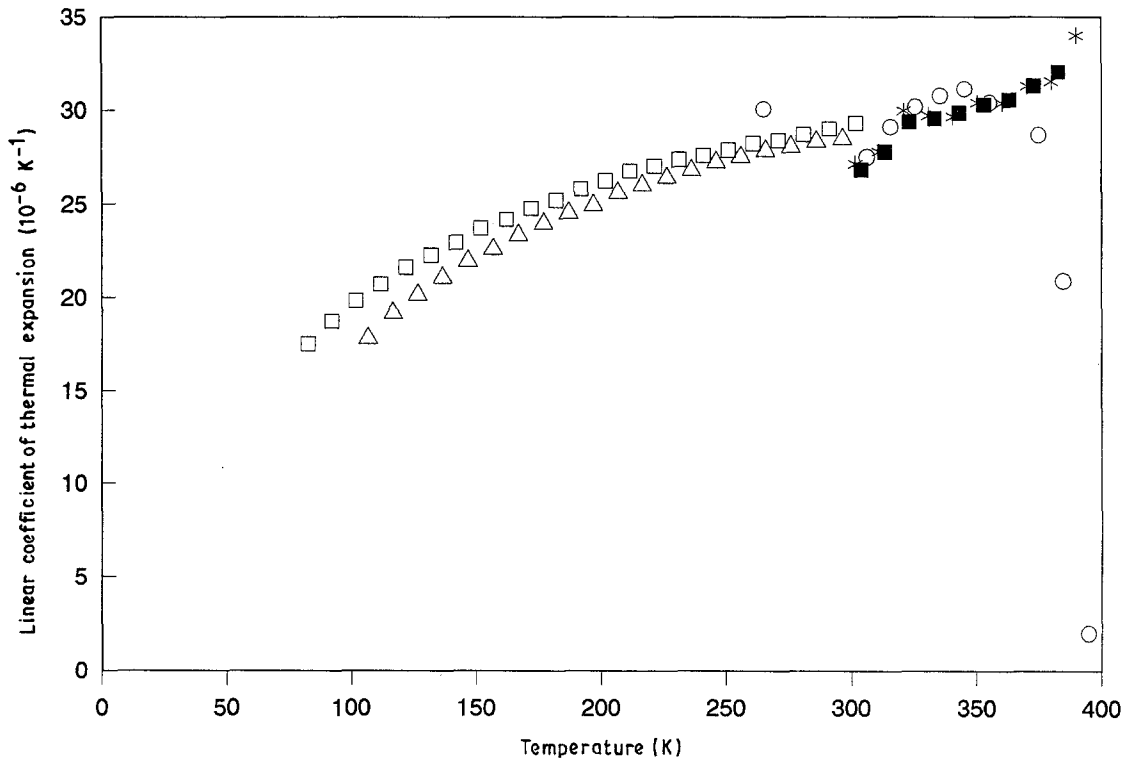


Figure 9 Variation with temperature of linear CTE at 90° to the fibre direction due to free volume annealing, AS4/PEEK. Best fit curve, 80–300 K: $\alpha = (-1.41 \times 10^{-5} T^2 + 0.0172T + 0.317) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (□) 1, (△) 2; high-temperature runs: (○) 1, (*) 2, (■) 3.

TABLE IV Measured change in linear CTE with relative fibre orientation, AS4/PEEK

	Angle relative to fibre orientation (deg)						
	10	20	30	40	50	80	90
Linear CTE ($\times 10^{-6} \text{ K}^{-1}$) at 296 K	1.35	3.00	7.15	13.43	16.03	30.40	30.19

TABLE V Change in linear CTE with relative fibre orientation, two-directional laminates, AS4/PEEK

	Included angle between plies (deg)							
	0	20	40	60	80	100	120	160
CTE ($\times 10^{-6} \text{ K}^{-1}$) at 296 K	0.24	-0.82	-2.42	-2.27	0.73	5.36	9.77	27.26

5.3. Through-thickness experiments

Owing to the small size of many of the samples used in this series of tests the data collected were found to be subject to significant scatter. Within the limits of accuracy of the experiment an increase of approximately 10%–15% was observed in $[+40/-40]_{4S}$ laminates over unidirectional material. Accurate measurements were carried out on two laminates, unidirectional and $[-45/45/0/90]_{5S}$ quasi-isotropic. This allowed for an assessment of both the change in behaviour caused by small differences in fibre/resin distribution through the thickness of a laminate, and that due to in-plane restraint effects. A summary of results for these laminates is presented in Table VI.

In order that the data produced from the series of experiments described above can be interpreted, it is necessary to examine them both in relation to each other and in comparison with theoretical models of behaviour. In all cases composite behaviour was consistent, and logical comparison of different material types is possible. For the case of AS4/PEEK composite, a body of data was produced which allowed comparison of experiment and theory, and this is discussed in the next section.

6. Discussion

It is most convenient to break the discussion into two discrete sections, one covering measurements carried out parallel to the fibre direction, and a second considering the performance of laminates in other directions.

6.1. Measurements parallel to the fibre direction

The behaviour of graphite fibre-reinforced composites shown in Figs 2–6 illustrates the constraining effect that negative CTE reinforcements have upon a positive CTE matrix. In all cases the basic shape of the curve is similar: at low temperatures the response of the fibres is predominant, with increasing temperature resulting in a reduction in the absolute value of CTE. As the temperature rises above approximately 200 K

TABLE VI Change in through-thickness thermal expansion behaviour with laminate type

Sample	Through-thickness Linear CTE ($\times 10^{-6} \text{ K}^{-1}$) at 296 K
Unidirectional	32.13
(Unidirectional, in plane)	(30.19)
$[+40/-40]_{4S}$	35.32
$[-45/45/0/90]_{5S}$	42.57

the thermal expansion of the composite begins to increase, suggesting that the matrix is beginning to affect more significantly the response of the material. The composite CTE continues to increase as the temperature approaches T_g for the polymer (416 K), although measurement ceased before this point was reached. The results of an earlier study [11] showed that beyond T_g the composite CTE falls and becomes negative as the resin softens, and therefore is less able to restrain fibre shrinkage; however, interpretation of results above the glass transition temperature of the polymer is difficult, because it is possible that the material is then affected by the mass of the experimental apparatus.

Figs 2–5 show the behaviour of composites containing reinforcing fibres of increasing stiffness: it is apparent that in moving from AS4 to P100 composite the CTE becomes increasingly negative, with IM7 fibres producing an expansion coefficient which hovers around zero. The response of the two pitch-fibre-reinforced composites is at all times negative (Figs 4 and 5) and very similar, due to the differing fibre contents: that of P75/PEEK was 55% by volume, whilst that of the P100/PEEK was 45%.

Using Equation 1 it is possible to estimate the linear coefficients of thermal expansion of the fibres themselves, and these are presented in Table VII: the values shown are in reasonable agreement with those in the manufacturer's data sheets, though the AS4 value is possibly a little low. This allows us to plot the change in fibre CTE with axial stiffness as shown in Fig. 10. The implication of the relationship shown is that

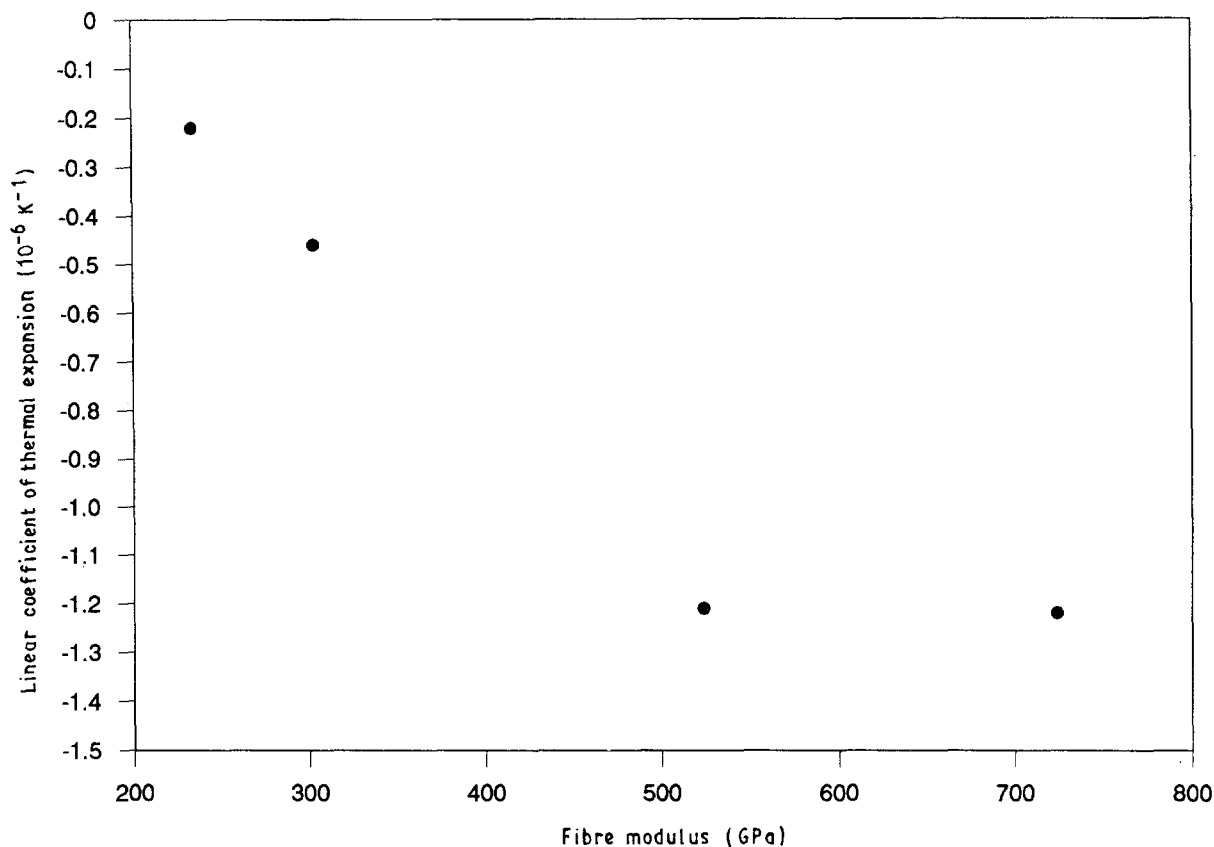


Figure 10 Change in calculated fibre CTE with axial modulus.

significant increases in fibre modulus above 724 GPa will have little effect upon CTE of the fibre, reflecting the purity of the graphitic structure in Thornel P100 fibre.

The behaviour of a composite in which no fibre/matrix bonding exists is shown in Fig. 6. The experimental fibre used in this material is essentially identical to AS4 in mechanical properties, but is treated such that no interfacial bonding occurs. The result shown in Fig. 6 is rather surprising, in that it is identical to that for the AS4/PEEK composite shown in Fig. 2. The implication of this result is that the thermal expansion behaviour of a unidirectional carbon-fibre composite parallel to the reinforcement does not depend solely upon interfacial bonding, but may be controlled simply by the shrinkage stresses and interfacial friction forces which are inherent in the material. The magnitude of normal pressure on fibres produced by thermal effects in carbon fibre/thermoplastic composites has been examined by Di Landro [13]. For a single cylindrical inclusion in a body of material, the normal stresses generated during cooling are given by the relation

$$\frac{(\alpha_m - \alpha_f^t)\Delta T E_m}{(1 + \nu_m) + (1 - \nu_f)(E_m/E_f)} \quad (10)$$

where the superscript t denotes transverse fibre properties and ΔT is the temperature difference from the 'stress free' temperature.

Using the properties in Tables I, VIII and IX, we may deduce a normal pressure of the order of 10 MPa. This is smaller than the values quoted for polyethersulphone and polyetherimide in [13], due to the rather low value for transverse CTE of fibres quoted in that

TABLE VII Calculated fibre CTE at 296 K

Reinforcement	Calculated linear CTE ($\times 10^{-6} \text{ K}^{-1}$) at 296 K
S-Glass	3.15
Hercules AS4	-0.22
Experimental fibre	-0.22
Hercules IM7	-0.46
Thornel P75	-1.21
Thornel P100	-1.22

TABLE VIII Calculated fibre transverse CTE at 296 K

Reinforcement	Calculated linear CTE ($\times 10^{-6} \text{ K}^{-1}$) at 296 K		
	Chamberlain [2]		Shapery [3]
	Square packing model	Hexagonal packing model	
S-Glass	14.0	10.0	16.8
Hercules AS4	26.6	24.1	36.3
Hercules IM7	26.0	23.4	38.7
Thornel P75	25.3	21.4	40.7

TABLE IX PEEK mechanical properties at 296–353 K

E (GN m^{-2})	ν_{12}	CTE [17] ($\times 10^{-6} \text{ K}^{-1}$)
3.8	0.4	47–55

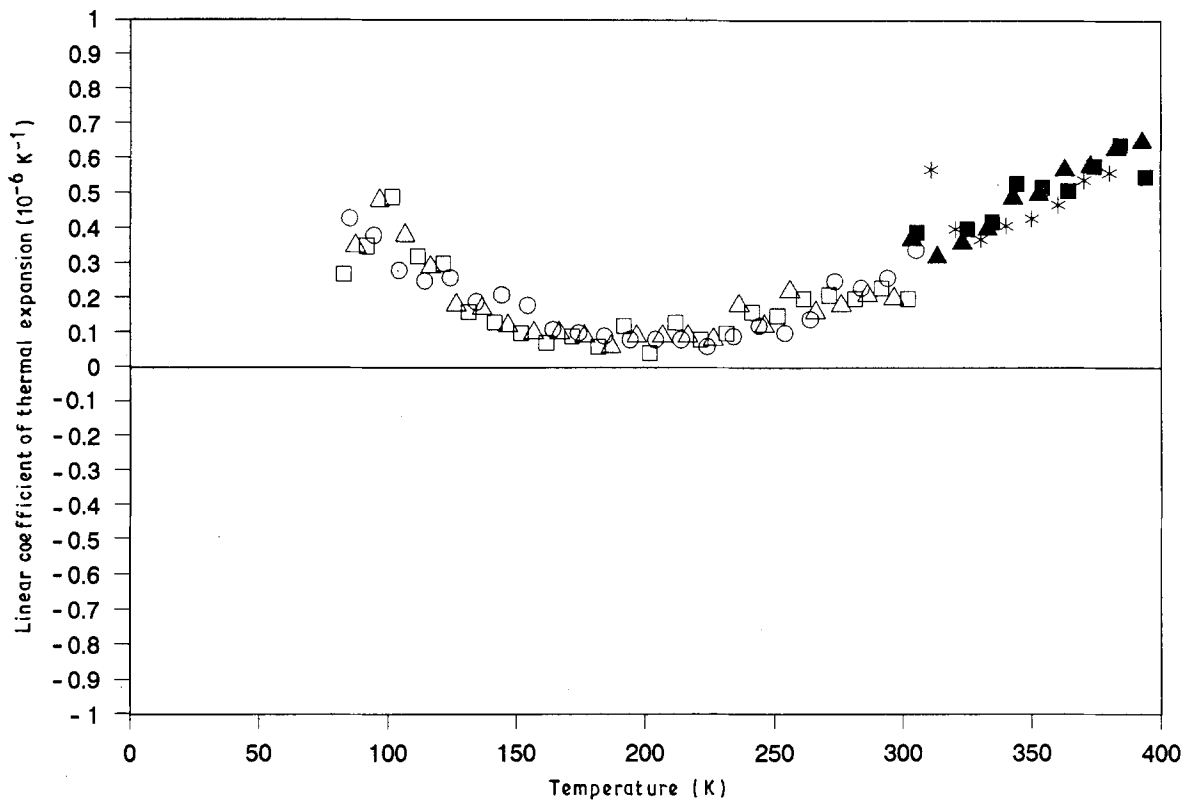


Figure 11 Change in linear CTE parallel to the fibre direction, AS4/PEEK after 10 thermal cycles. Best fit curve, 80–300 K: $\alpha = (2.47 \times 10^{-5} T^2 - 0.0101T + 1.106) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (\square) 1, (\triangle) 2, (\circ) 3; high-temperature runs: ($*$) 1, (\blacksquare) 2, (\blacktriangle) 3.

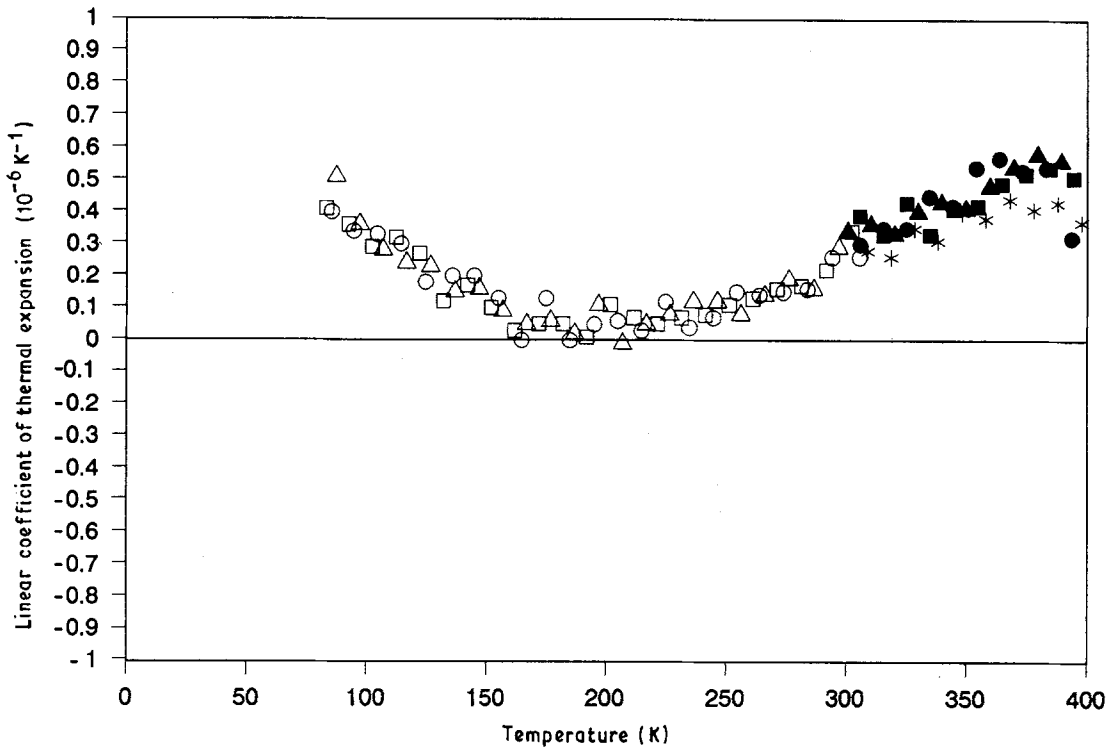


Figure 12 Change in linear CTE parallel to the fibre direction, AS4/PEEK after 100 thermal cycles. Best fit curve, 80–300 K: $\alpha = (2.63 \times 10^{-5} T^2 - 0.0109T + 1.167) \times 10^{-6} \text{ K}^{-1}$. Low-temperature runs: (\square) 1, (\triangle) 2, (\circ) 3; high-temperature runs: ($*$) 1, (\blacksquare) 2, (\blacktriangle) 3, (\bullet) 4.

work. However, surface roughness of carbon fibres is such that this is likely to result in efficient pinning of fibres [13], and hence prevent changes in CTE of bonded and unbonded fibre composites. Note that this does not automatically imply that high T_g composites will have high resistance to thermal expansion hysteresis, because shear stresses set up at the fibre–

matrix interface may work against the compressive forces.

Although the low-hysteresis result may not follow for multidirectional laminates in which interply stresses will exist, it does indicate that AS4/PEEK composites with a well-bonded interface are likely to be highly resistant to the effects of repeated thermal

cycling. In order to test this assertion a number of AS4/PEEK samples were cycled repeatedly over the temperature range 113–393 K by Composite Optics Inc., San Diego. The interferometrically determined CTE response of specimens cycled 10 and 100 times is shown in Figs 11 and 12. Comparison with the behaviour of virgin material in Fig. 2 reveals that within the limits of accuracy of the experiment the behaviour is invariant. This is a powerful result and parallels early work done on similar developmental materials, which showed the composite to be hysteresis-free in thermal expansion behaviour between 296 and 373 K [14]. It is intended that a similar study will be carried out using cross-plyed laminates, in order to assess the effects of internal residual macroscopic stress on thermal expansion hysteresis.

6.2. Measurements away from the fibre direction

6.2.1. Unidirectional laminates

In order to allow for a complete characterization of the materials involved in this study which are commercially available, measurements were taken at angles away from the primary reinforcement, as described above. Laminate behaviour was in all cases smooth and reproducible, with little change in CTE with temperature being noted: numerical data are presented in Tables III and IV. Measurements carried out at 90° to the fibre direction allow calculation of apparent CTE values for the fibres in the transverse direction; the results calculated using Equations 2 and 3 are presented in Table VIII. Using Equation 2 due to Chamberlain, reasonable agreement with the results of other workers has been achieved, but note that the results calculated using the Shapery and Chamberlain relationships differ by between 50% and 100%, depending upon initial assumptions. Because these relationships are those usually used for back-calculation of fibre transverse CTE, it is impossible to ascertain which is “correct”; one would usually expect to observe better agreement, and one possible conclusion is that one of the data required for the calculations is in error. However, it is interesting to note that both of the approaches give values for the transverse coefficient of thermal expansion of glass fibres which are significantly greater than those calculated parallel to the reinforcement direction (Tables VII and IX). Because glass fibres are usually assumed to be isotropic in terms of their mechanical and thermal properties, the implication is that the analyses are inaccurate. This observation is confirmed in part by the work of Sheaffer [15], who carried out direct measurements of transverse fibre behaviour by means of laser diffraction, and observed coefficients of thermal expansion for Hercules PAN fibre approximately 50% smaller than those calculated here. Because this discrepancy is typical for other carbon fibre-reinforced composites, it is clear that this is an area worthy of further study.

The results shown in Table VI for comparative properties of unidirectional laminates in-plane and out-of-plane indicate that within the level of accuracy of the apparatus an increase in expansion of the

laminate through the thickness can be detected. This small change (less than 10%) is due to a variation in fibre-resin distribution through the thickness of the laminate. During fabrication, neighbouring plies of composite do not interpenetrate, but rather form separate layers bounded by thin (typically 3 μm) regions of pure resin. The value of CTE measured in the range 293–303 K is close to that predicted for an unconstrained hybrid material consisting of thin layers of PEEK and layers of reinforced polymer with slightly raised fibre content.

Using the results in Table III and the data generated for laminate behaviour in the fibre direction, it is possible to predict the response of a unidirectional laminate at any angle to the fibres using Equation 5. The upper curves in Figs 13–15 show the predicted response of the AS4, IM7 and glass-reinforced PEEK composites involved in this study. Fig. 13 also includes the experimental data generated for off-axis behaviour of the AS4/PEEK. Good agreement is achieved between experiment and theory. Based on this observation, it is reasonable to assume that glass and IM7 composites will also exhibit good agreement with theory.

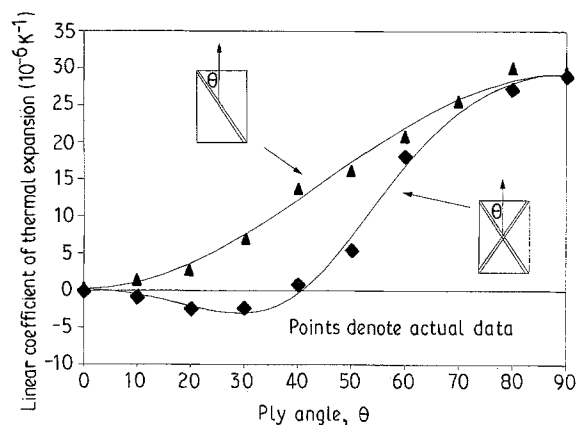


Figure 13 Linear CTE of AS4/PEEK laminates at 296 K (predicted and measured).

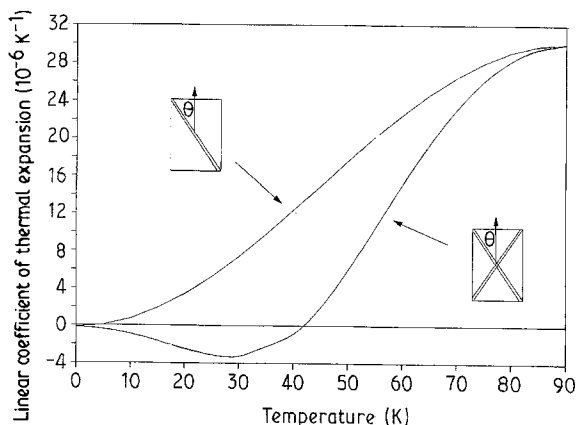


Figure 14 Linear CTE of IM7/PEEK laminates at 296 K (predicted).

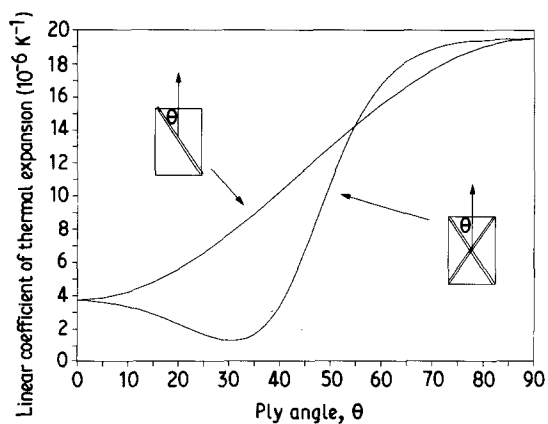


Figure 15 Linear CTE of S2 glass/PEEK laminates at 296 K (predicted).

6.2.2. Bidirectional laminates

Using classical laminate theory the thermal expansion behaviour of multidirectional composite laminates can be predicted given mechanical property data and the thermal expansion coefficients of unidirectional laminates. The predicted behaviour of bidirectional laminates in the direction bisecting the angle between the fibres is shown in the lower curves in Figs 13–15.

The response shown is characteristic of angle ply laminates, where the combination of two plies with positive CTE in both directions may result in a negative CTE in a laminate with small angular ply separation. This result is due to the fact that the fibres are essentially inextensible, and the large CTE which results in such a laminate in the *Y*-direction forces a reduction in length in the *X*-direction. It is important to note that the laminate behaviour is dependent upon the CTE values of unidirectional material, and upon the mechanical properties of the composite: hence the CTE of a multidirectional specimen is likely to change with temperature. This is a fact often missed when “zero CTE” laminates are produced, and it is important to specify the temperature range over which this “zero CTE” occurs.

The expansion behaviour of AS4/PEEK laminates of the form $[\pm \theta]_{4S}$ was examined in order to test that the theoretical predictions of behaviour were accurate. In all cases the response was consistent and reproducible, with a small increase in absolute value with increasing temperature in most cases; properties at 296 K are shown in Table V. These data are compared with the predicted values for this material in Fig. 13, and once again excellent agreement is apparent. It is likely that most of the other thermoplastic laminates studied in this work will also behave in a similar manner, and hence detailed experimental examination of their behaviour is probably unnecessary. This assertion does not hold for PEEK composites produced using Thornel P75 and P100 fibre, because such materials are likely to exhibit transverse microcracking when the included angle between the plies approaches 90° [16], and further study would be required to explore fully the magnitude of any effects.

The through thickness behaviour of off-axis laminates summarized in Table VI indicates that multidirectional composite laminates have a coefficient of thermal expansion greater than that of unidirectional composite. Using Equation 6 it is possible to show that the through thickness CTE of a $[\pm 40]_{4S}$ AS4/PEEK laminate should be approximately $38 \times 10^{-6} \text{ K}^{-1}$ at room temperature, which compares reasonably with the measured property. This measurement was carried out on a laminate with a thickness of only 1 mm, which is inherently unsatisfactory given the small magnitude of the dimensional changes involved. The only thicker non-unidirectional laminates available at the time of this study were quasi-isotropic of the form $[-45/45/0/90]_{5S}$, and in consequence Equation 6 cannot strictly apply. However, the expression will provide a lower bound for the through-thickness CTE value, which for AS4/PEEK can be shown to be $38.7 \times 10^{-6} \text{ K}^{-1}$ at room temperature; hence the value for the thick quasi-isotropic laminate quoted in Table VI appears reasonable. This section of the study is incomplete, and further work is required to elucidate fully the behaviour of these materials in the through-thickness direction.

7. Conclusions

From the results presented in this study the following conclusions may be drawn.

1. The thermal expansion behaviour of unidirectionally reinforced PEEK composites is heavily dependent upon that of the fibres.

2. Calculated values of fibre CTE based on the performance of unidirectional PEEK laminates are in satisfactory agreement with data from other workers.

3. In the case of graphitic (carbon or pitch) fibre, increasing fibre modulus results in increasingly negative CTE for the composite.

4. Parallel to the fibre direction, AS4/PEEK has a positive, near-zero CTE in the temperature range 83–393 K: IM7-reinforced material displays negative CTE in the centre of this range.

5. Pitch fibre/PEEK composites display negative CTE parallel to the fibre direction in the temperature range 83–393 K.

6. The behaviour of glass-reinforced PEEK differs significantly from that of polymer with graphitic reinforcement, and is positive at all times over the temperature range examined.

7. The shrinkage stresses which are set up during production of AS4/PEEK composite are sufficiently large to overcome the interfacial shear stresses due to the difference in coefficient of thermal expansion of fibre and matrix.

8. The predicted CTE behaviour of both unidirectional and multidirectional AS4/PEEK composites shows good agreement with experimental data: it is expected that glass- and IM7-reinforced material will also behave as predicted.

9. The models of Shapery and Chamberlain, commonly used for the calculation of fibre behaviour from composite performance, are significantly in error.

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