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The thermal expansion of carbon fibre reinforced plastics

Part 3 *The influence of resin type*

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Interferometric measurements of the linear thermal expansion coefficients of epoxy resin Code 69 are reported over the approximate temperature range 90 K to 500 K. Corresponding measurements on specimens of this resin reinforced with unidirectional Courtaulds HTS carbon fibre and on specimens of resins DLS $351/BF_3400$ and Code 69 reinforced with bidirectional HTS fibres are also reported. The results are qualitatively similar to earlier observations on similar specimens based upon ERLA 4617/*m*PDA and DLS $351/BF_3400$ resins. A comparison of the present results with those described earlier has established that a detailed knowledge of the temperature dependence of the thermal expansion characteristics of a resin permits a good estimate to be made of the corresponding behaviour of unidirectional and bidirectional composites based upon it.

1. Introduction

Experimental data emerging from a recent systematic study of the thermal expansion characteristics of a series of carbon fibre reinforced epoxy resins (CFRP) lend themselves to appraisal within the framework of theoretical models of the thermoelastic behaviour of two-phase composites. The data were applied in Part 1 of this series to study the influence of fibre type and orientation [1] and in Part 2 to examine the influence of fibre volume fraction [2].

The resin system upon which most of the latest specimens in the programme were based, Code 69‡, differs from those employed in Part 1 (ERLA 4617/*m*PDA) and Part 2 (DLS $351/BF_3400$), so that in addition to their direct technological interest these latest results may be included with the earlier data to obtain an understanding of the influence of the resin on the thermal expansion of the composite.

In the account which follows, direct reference is made to the graphs and specimen designations in Parts 1 and 2. The description of the new data is followed by a comparative survey in which the only deliberate variable is the resin system. By using the same fibre (Courtaulds HTS) and by employing the same apparatus throughout, it is believed that the data form a basis for firm conclusions concerning the influence of some of the many variables which are encountered in components constructed from these materials.

2. The specimens

Because of interest in the Code 69 system within the aerospace industry, experimental thermal expansion data for unidirectional composite specimens based upon it were augmented by measurements upon specimens prepared from cross-plied laminates having inter-ply angles of 90° and 63°. Details of the specimens and the bars from which they were cut are given in Table I.

The resin from which bar 12 was made was received from the manufacturers as a solution. This was out-gassed in a vacuum dessicator for

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TABLE I The specimens

Bar number	Specimen designation	Resin type	Angle between fibre directions (°)	Direction of thermal expansion measurements	Fibre volume (%)	Void content (%)
12	25	Code 69			0.0	0.0
13	26	Code 69	0	Parallel to fibres	58.9	0.0
13	27	Code 69	0	Perpendicular to fibres	58.9	0.0
14	28	Code 69	90	In plane of laminate	58.9	0.0
14	29	Code 69	90	Perpendicular to plane of laminate	58.9	0.0
15	30	Code 69	63	Bisecting acute angle	57.0	0.0
15	31	Code 69	63	Bisecting obtuse angle	57.0	0.0
15	32	Code 69	63	Perpendicular to plane of laminate	57.0	0.0
16	33	DLS 351	90	In plane of laminate	61.4	1.8
16	34	DLS 351	90	Perpendicular to plane of laminate	61.4	1.8

several days to remove the solvent. The resin was then transferred to a 100 x 12 mm steel bar-mould, placed in a vacuum oven at 75° C and out-gassed for several hours to remove solvent and air. The vacuum was then released and the temperature raised to 100° C for 2 hours, to 170° C for 1 hour and to 200° C for a further 5 hours. The ends of the mould were loosened before cooling down to allow the laminate to expand freely.

Bar 16 was prepared from aligned tows of Courtaulds HTS fibre Batch PT112/21Z and DLS 351/$BF_3$400 resin by the standard technique and curing cycle described earlier [1, 2].

Sets of three specimens were cut from the bars in each of the required directions. During a later stage of the programme the carborundum-loaded tungsten wire saw used for cutting the specimens was replaced by a diamond-loaded stainless steel disc saw (model Macrotome 2 manufactured by Metals Research Ltd) lubricated with Avigrinde 80. This had the advantage of cutting faster without overheating the specimens.

In Part 1 it was explained how calculations had indicated that the linear thermal expansion coefficients in the two directions parallel to the fibres of a 13 layer–12 layer alternated 0°–90° cross-plied laminate were expected to differ by about 10 per cent. Although subsequent measurements revealed that this was no greater than the variation observed with position within a bar, the practice of grinding away half of each outer ply layer was adopted in preparing the specimens for the measurements reported in this paper in order to produce balanced laminates with an equal number of fibres in each direction.

Also in Part 1 it was explained how differences between the linear thermal expansion coefficients of specimens cut parallel to the fibres of 0°–90° laminates and specimens having their major axis bisecting the angle between the fibre directions did not assume significant proportions until temperatures were reached at which resin softening effects became apparent. For this reason only one set of in-plane measurements was undertaken upon each set of specimens from bars 14 and 16. Other details concerning the preparation and investigation of the specimens were the same as those described in Part 1.

3. Results

The primary data obtained from the latest measurements are displayed in Figs. 2 to 11, from which an idea of the experimental uncertainties may be gained. Smoothed data are summarized in Table II.

4. Discussion

4.1. Comparative considerations

It is instructive to compare the temperature dependencies of the linear thermal expansion coefficients of resins ERLA 4617/*m*PDA, DLS 351/$BF_3$400 and Code 69, and to see to what extent these allow the comparative behaviour of composites based upon them to be predicted.

4.1.1. Pure resin; specimens 1 (Part 1), 18 (Part 2) and 25.

The results for the three resins are compared in Fig. 1. The principal features may be summarized:

(a) The three sets of results are similar in magnitude and temperature dependence below room temperature.

(b) In Part 2 a discontinuity was reported in the thermal expansion results for DLS 351 in the neighbourhood of room temperature. A more complete examination of the results for this resin reveals also a change of slope between 427 K and

TABLE II Smoothed values of the linear thermal expansion coefficients of the specimens described in Table 1

T (K)	α for the specimens numbered below (K^{-1})									
	25	26	27	28	29	30	31	32	33	34
	($\times 10^{-5}$)	($\times 10^{-7}$)	($\times 10^{-5}$)	($\times 10^{-6}$)	($\times 10^{-5}$)	($\times 10^{-6}$)	($\times 10^{-5}$)	($\times 10^{-5}$)	($\times 10^{-6}$)	($\times 10^{-5}$)
90	2.20	−0.8	1.30	1.56	1.92	−1.00	0.78	1.80	1.29	1.87
100	2.30	−0.8	1.39	1.58	2.02	−1.10	0.81	1.90	1.33	1.96
120	2.51	−0.9	1.55	1.63	2.22	−1.37	0.89	2.09	1.41	2.17
140	2.73	−1.2	1.70	1.68	2.41	−1.66	0.96	2.24	1.47	2.37
160	2.95	−1.8	1.84	1.73	2.60	−1.92	1.03	2.45	1.53	2.57
180	3.16	−2.4	1.97	1.78	2.79	−2.18	1.10	2.62	1.59	2.76
200	3.37	−2.6	2.09	1.85	2.98	−2.39	1.18	2.81	1.67	2.96
220	3.58	−2.4	2.21	1.92	3.17	−2.59	1.25	3.00	1.77	3.15
240	3.78	−1.9	2.31	1.99	3.35	−2.76	1.32	3.19	1.88	3.33
260	3.97	−1.1	2.41	2.05	3.55	−2.90	1.39	3.36	2.03	3.50
280	4.17	−1.0	2.51	2.13	3.75	−3.02	1.47	3.54	2.18	3.66
300	4.39	−2.0	2.60	2.21	3.91	−3.18	1.54	3.71	2.24	3.81
320	4.63	−3.9	2.69	2.30	4.10	−3.27	1.61	3.99	2.23	3.95
340	4.90	−4.0	2.78	2.39	4.29	−3.37	1.68	4.28	2.14	4.08
360	5.20	−3.2	2.86	2.50	4.49	−3.42	1.75	4.64	2.02	4.19
380	5.54	−1.9	2.98	2.61	4.70	−3.50	1.83	5.08	1.98	4.29
400	5.91	0.1	3.11	2.74	4.95	−3.56	1.90	5.35	2.07	4.47
420	6.36	2.1	3.27	2.90	5.25	−3.70	1.97	5.52	2.26	4.70
440	6.91	2.6	3.51	3.16	5.59	−4.03	2.05	5.77	2.68	5.04
460	7.57	2.3	3.85	3.56	6.02	−4.65	2.12	6.40	3.16	5.61
480	8.38	1.0	4.44	4.21	6.68	−6.22	(2.19)	8.64	3.40	6.50
490	8.92	0.1	4.97	3.80	7.20	−8.65		10.9	2.95	7.09
500	(9.50)	−1.2		2.66	8.23			13.7	2.28	7.89
510				1.53				17.5	1.59	9.09
520				0.44					0.72	

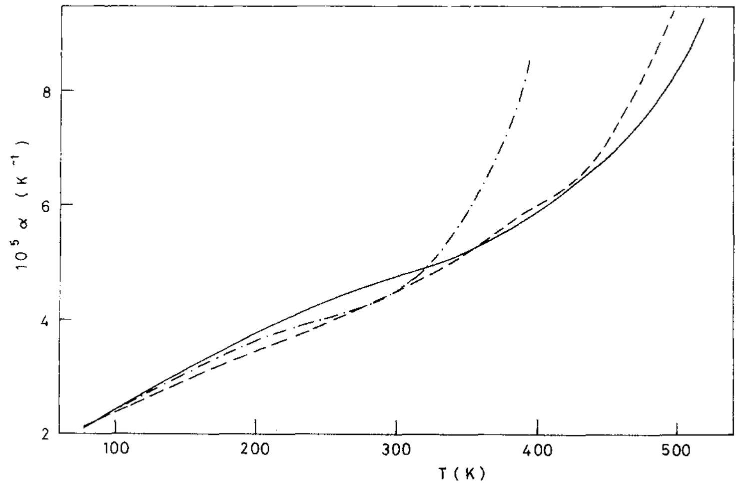


Figure 1 The linear thermal expansion coefficients of three epoxy resins; comparison of smoothed results. —·—·— ERLA 4617/*m*PDA (specimens 1) ——— DLA 351/$BF_3$400 (specimens 18) – – – – Code 69 (specimens 25).

473 K. Differential scanning calorimetry measurements were carried out on samples of the resin bars; the results were in general accord with the above effects and it was concluded that changes in the internal degrees of freedom of the resin structure were occurring between approximately 300 and 350 K and that the glass transition temperature was approximately 450 K. Examination of the primary thermal expansion data for Code 69 (Fig. 2) reveals the existence of a similar discontinuity in the vicinity of room temperature. This is also associated with an endothermic transition found in the corresponding differential scanning calorimetry measurements and centred

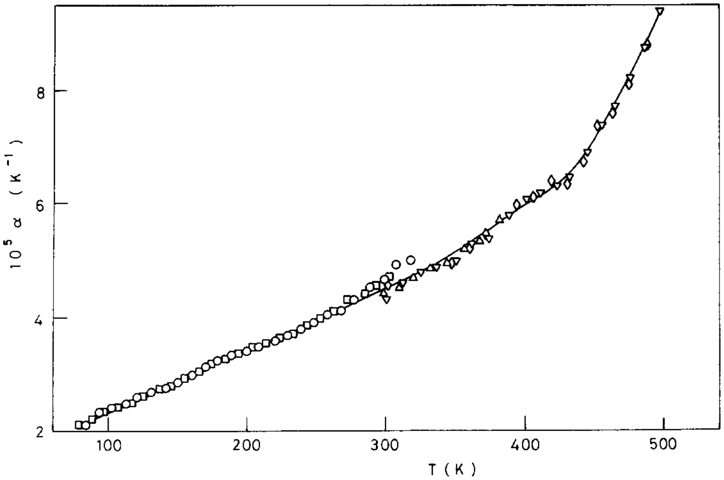


Figure 2 The linear thermal expansion coefficient α of specimens 25: ○ run 1; □ run 2; △ run 3; ▽ run 4; ◇ run 5.

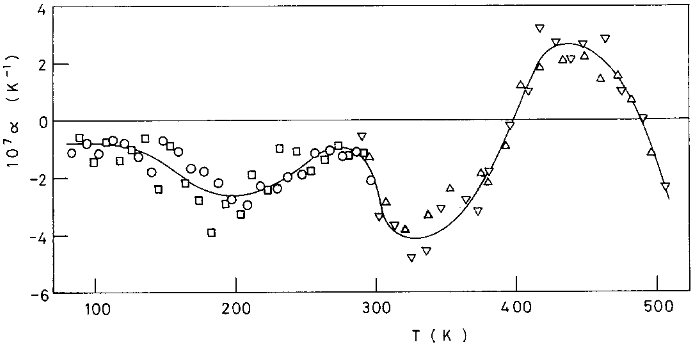


Figure 3 The linear thermal expansion coefficient α of specimens 26: ○ run 1; □ run 2; △ run 3; ▽ run 4.

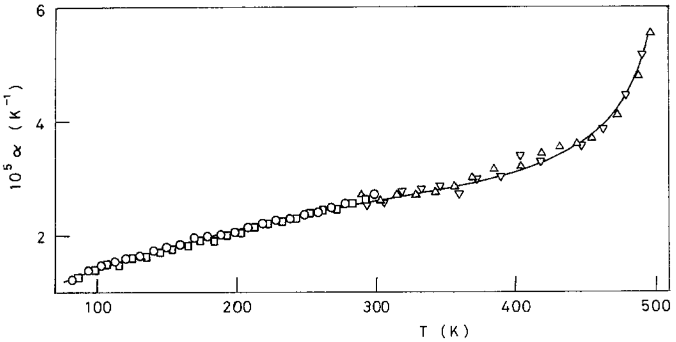


Figure 4 The linear thermal expansion coefficient α of specimens 27: ○ run 1; □ run 2; △ run 3; ▽ run 4.

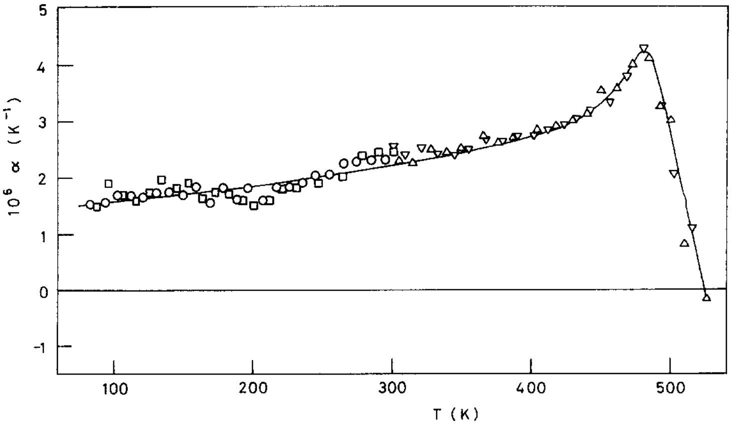


Figure 5 The linear thermal expansion coefficient α of specimens 28: ○ run 1; □ run 2; △ run 3; run 4.

around 320 K. The DSC measurements also indicate that the glass transition temperature of Code 69 is approximately 507 K, which lies just above the highest temperatures at which the stability of the interference fringes permitted thermal expansion to be measured. Detailed comparison with the corresponding results for ERLA 4617/*m*PDA is prevented by the shortage of experimental data.

(c) Above room temperature the results for DLS 351 and Code 69 are mutually similar but differ from those of ERLA 4617, which show a much more rapid increase in the coefficient of expansion, commencing at a significantly lower temperature.

4.1.2. Unidirectional bars, 60% HTS fibre, parallel to the fibre direction; specimens 21 (DLS 351) and 26 (Code 69)

The only intentional difference between these specimens lies in the identities of the resins. Comparing the results for specimens 21 (Part 2, Fig. 4) with the results for specimens 26 (Fig. 3 of the present paper), the broad features of the two sets of results may be seen to be qualitatively similar to each other and to those for the ERLA 4617 unidirectional specimens 2 (HTS fibres) and 10 (HMS fibres) reported in Part 1. A similar explanation to that advanced previously in terms of the predominating influence of the fibres and resin in different temperature ranges appears to apply. On the other hand, the pronounced dip observed in the results for specimens 21 and 26 just above room temperature is not seen in the results for the ERLA 4617 based specimens 2 and 10. Although it would be unwise to elaborate upon this difference in view of the less complete coverage of this temperature region in the earlier work, the dips in the results for specimens 21 and 26 coincide in temperature with those observed in the cases of the corresponding pure resins, i.e. specimens 18 and 25, and the two pairs of results are each self-consistent in the sense of the change in α with rising temperature. The main difference between the results for specimens 21 and 26 lies in the magnitude and position of the minimum which occurs below room temperature. In view of the similarity of the thermal expansion coefficients of the resins one may tentatively conclude that the shallower dip may be caused by the Young's modulus of Code 69 exceeding that of DLS 351/$BF_3$400 in this low temperature region although direct measurements indicate that the opposite is true at ambient temperature.

4.1.3. Unidirectional bars, 50% HTS fibre, parallel to the fibre direction; specimens 2 (ERLA 4617) and 19 (DLS 351)

In this consideration of the specific influence of the resin, it is appropriate that the results for these unidirectional bars containing nominally identical fibre volume fractions of HTS fibres taken from the same batch should be examined again. It may be concluded that:

(a) The results for specimens 2 (Part 1, Fig. 3) and 19 (Part 2, Fig. 2) are qualitatively similar.

(b) Corresponding features in the results for

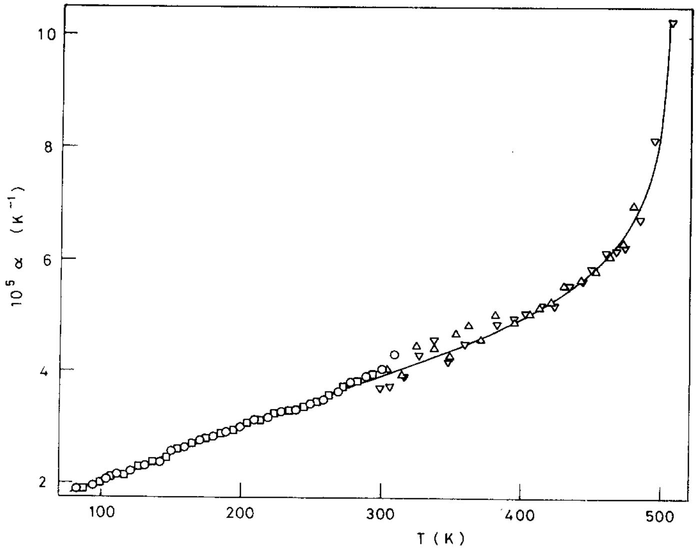
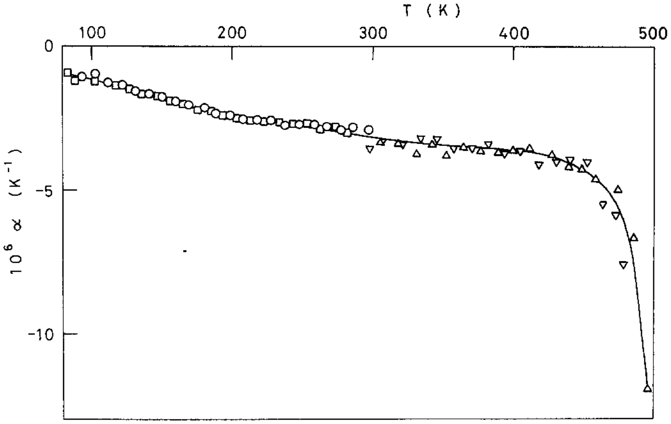


Figure 6 The linear thermal expansion coefficient α of specimens 29: ○ run 1; □ run 2; △ run 3; ▽ run 4.

Figure 7 The linear thermal expansion coefficient α of specimens 30: ○ run 1; □ run 2; △ run 3; ▽ run 4.



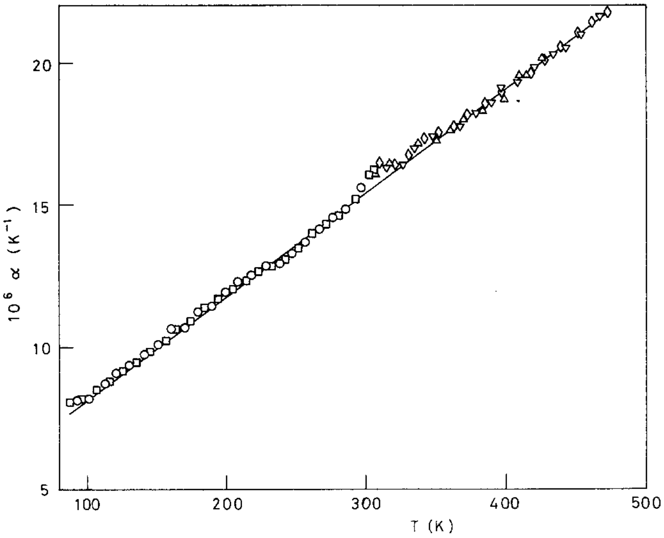


Figure 8 The linear thermal expansion coefficient α of specimens 31: ○ run 1; □ run 2, △ run 3, ▽ run 4.

specimens 19 are displaced towards less positive values of α than those of specimens 2.

(c) The final sharp decrease in α with rise of temperature occurs at a temperature 80 to 90 degrees higher for the DLS 351 composite.

4.1.4. Unidirectional bars, 60% HTS fibre, Perpendicular to the fibre direction; specimens 22 (DLS 351) and 27 (Code 69)

The results for these two sets of specimens, displayed in Fig. 5 of Part 2 and Fig. 4 of the present paper, are almost identical at all temperatures. In view of the similarity of the thermal expansion coefficients of the resins upon which they are based and the nominal identities of the fibres and their volume fractions, this similarity is not surprising. On the other hand, the absence of a significant difference between the two sets of results in the neighbourhood of 150 K for these transverse specimens contrasts with the difference observed between the results for the parallel-oriented specimens 21 and 26. The linear thermal expansion coefficient of pyrolytic graphite in a direction parallel to the c-crystallographic axis [3], is similar to the value for Code 69 resin in this temperature region. Hence if the linear thermal expansion coefficient of the carbon fibres in the direction perpendicular to their length is of the same order of magnitude, the stresses due to thermal mismatch in the transverse direction of a unidirectional bar of CFRP will be much smaller than those in the direction of the fibre axes. Herein, presumably, lies the origin of the contrasting comparisons.

4.1.5. Unidirectional bars, 50% HTS fibre, perpendicular to the fibre direction; specimens 3 (ERLA 4617) and 20 (DLS 351)

These results are shown in Part 1, Fig. 4 and Part 2, Fig. 3. The minor differences between the results

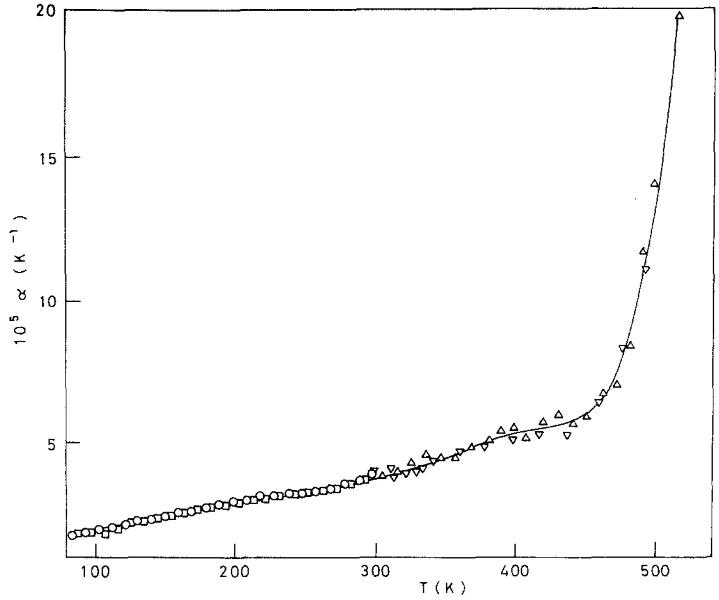


Figure 9 The linear thermal expansion coefficient α of specimens 32: ○ run 1; □ run 2; △ run 3; ▽ run 4.

below ambient temperature for the two different resin systems are no greater than would be expected to occur between nominally identical composites as a result of small variations in manufacture. More striking is the pronounced rise in the results for the ERLA 4617 based specimens, which commences about 50° below the corresponding rise in the results for the DLS 351 based specimens. This is consistent with the behaviour of the two pure resins (Section 4.1.1.).

4.1.6. Cross-plied bars, 60% HTS fibre, in plane of laminate; specimens 28 and 33.

The most striking feature of the in-plane results for the alternated 0°–90° cross-plied laminates based upon resins DLS 351 (Fig. 5) and Code 69 (Fig. 10) is their similarity. This is compatible with the closely similar results for the pure resins; small differences between the smoothed results are within the limits of variations expected on grounds of departure from constructional ideality.

The smooth curve drawn through the primary data in Fig. 5 does not take into account the undulations visible below 400 K. In Fig. 10, however, the curve has been drawn to follow the undulations because of their greater magnitude. The most pronounced undulations are consistent with those observed in the primary data for the pure resins.

4.1.7. Cross-plied bars, 60% HTS fibre, perpendicular to plane of laminate; specimens 29 and 34.

Similar remarks apply to the results corresponding to the direction perpendicular to the planes of the 0°–90° cross-plied laminates based upon Code 69, (Fig. 6) and DLS 351, (Fig. 11). The two sets of results are similar at all temperatures and the evidence for a departure from monotonic behaviour in the neighbourhood of room temperature is similar to that previously observed.

4.2. Additional results

The results for specimens 30, 31 and 32, which were cut from the Code 69 alternated 0°–63° cross-plied laminate constituting bar 15 are displayed in Figs. 7, 8 and 9. Remarks appropriate to an understanding of them resemble those advanced for the specimens cut from the corresponding directions of the 0°–63° ERLA 4617 laminates described in Part 1. Other features of the results, which are obvious upon inspection, correspond with features displayed by the results for the other specimens based on Code 69, upon which comments have already been made.

5. Summary and conclusions

A number of components constructed from CFRP operate over a temperature range in which stable physical characteristics are preferred. A prior

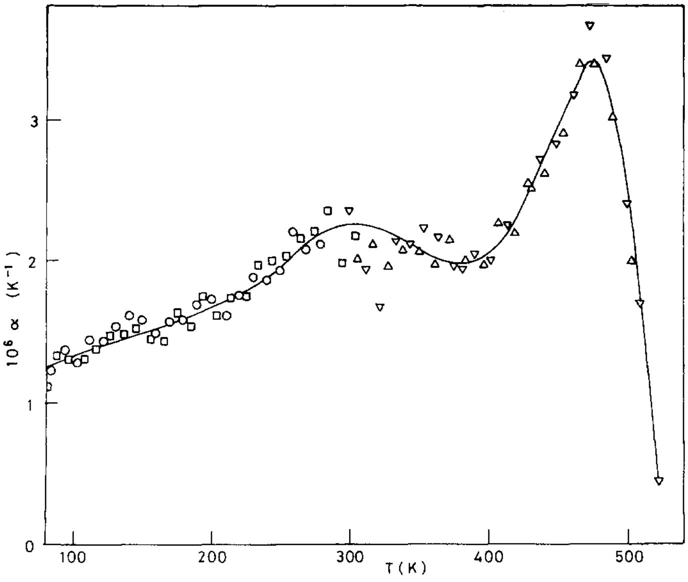


Figure 10 The linear thermal expansion coefficient α of specimens 33; △ run 1; ▽ run 2 for the first set of specimens; ○ run 1; □ run 2 for the second set of specimens.

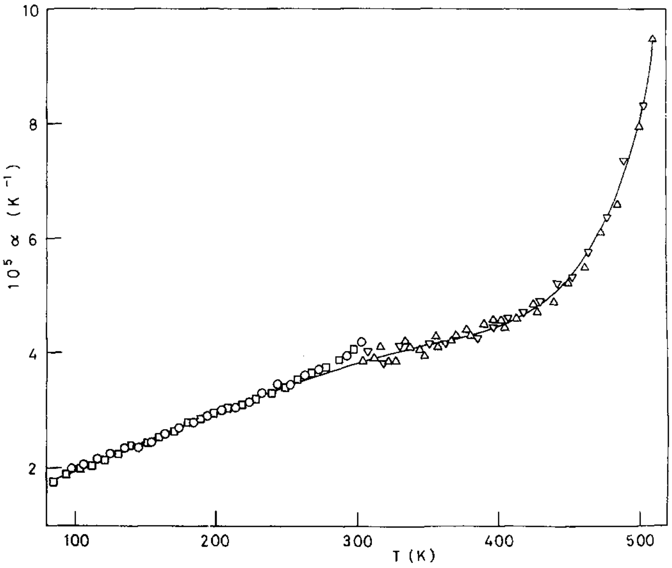


Figure 11 The linear thermal expansion coefficient α of specimens 34: ○ run 1; □ run 2; △ run 3; ▽ run 4.

evaluation based on the constituents of the composite calls for information concerning; (a) the linear thermal expansion coefficient of the resin, (b) the elastic constants of the resin, (c) the linear thermal expansion coefficients of the fibre, (d) the elastic constants of the fibre. The foregoing account, together with Parts 1 and 2, has provided data required under (a) above for three epoxy resins and has made it possible to demonstrate the extent to which the thermal expansion characteristics of the resins influence the corresponding characteristics of composites based upon them.

The results also show clearly how composites based upon resins DLS 351/$BF_3$400 and Code 69 may be employed at temperatures some 90° higher than those based on ERLA 4617/*m*PDA before the effects of resin softening become apparent. Finally, the rapid rise in the linear thermal expansion coefficients of cross-plied laminates in directions perpendicular to their planes clearly indicates the danger of causing high residual strains in complex CFRP structures by post-curing at too high a temperature.

The similarity of the linear thermal expansion coefficients and elastic constants of DLS 351/$BF_3$400 and Code 69 implies that the quantitative conclusions for Code 69 composites at room temperature must resemble those outlined for DLS 351/$BF_3$400 composites in Part 2. Recapitulating and summarizing, the qualitative agreement between the predicted and observed thermal characteristics of bidirectional carbon fibre reinforced plastics structures is good, and the quantitative agreement is as good as can reasonably be expected in view of the incomplete nature of some of the ancillary data required. An extension of the scope and temperature range of the ancillary investigations implied in (b), (c) and (d) above should provide the means of confirming and extending these conclusions.

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