JOURNAL OF MATERIALS SCIENCE 27 (1992) 5015–5026

Thermal expansion of phenolic resin and phenolic–fibre composites

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A large number of thermal expansion measurements in the temperature range 20 to 300 °C are presented for the Monsanto phenolic resin SC-1008 as a function of heating rate, position in cured block, curing treatment and repeated heating cycles. Thermal expansion measurements in those directions where the resin dominates are also reported up to 400 °C for composite systems consisting of the phenolic resin reinforced with ~60% (volume fraction) of either continuous unidirectional silica or bidirectional carbon (rayon precursor) fibres. The large variation in thermal expansion measurements is used to show that current curing treatments for the materials do not yield a resin with predictable expansion response. Annealing at a higher temperature (> 200 °C) than the maximum used in the curing treatments is shown to stabilize the phenolic resin SC-1008. Then, the mean linear coefficient of thermal expansion for the pure resin up to 100 °C is within the range $(55 \pm 5) \times 10^{-6}$ °C^{-1}.

1. Introduction

Directionally fibre-reinforced composite materials are finding increasing applications, both as structural materials [1, 2] and as ablatives for thermal protection systems [3, 4]. A prerequisite for successful structural design using such complex materials is a knowledge of the thermal expansion behaviour.

The thermal expansion of any fibre composite system for which the matrix is a polymer resin can be affected by many variables such as volume fraction of constituents, the type of resin and its wetting characteristics, fabrication parameters such as cure time, the residual thermal stress state, moisture absorption, the thermal history of the material and the relative moduli of the constituents. Surveys of the effect of such parameters on the expansion of epoxy resin composites reinforced with carbon fibres from − 180 to + 180 °C have already been reported [5–7]. One objective of the thermal expansion experimental programmes has been to use expansion data for pure resin and its composites to predict coefficients of thermal expansion for the reinforcing fibres along and perpendicular to their lengths. To realise this objective micro-mechanical models, as reviewed recently [8], provide the necessary theoretical models from which the required fibre properties can be obtained.

Phenolic resin composites with carbon or silica fibres possess excellent ablative properties and can be used in thermal protection systems for re-entry vehicles and rocket engine components [3]. It is desirable to know the expansion response of the constituent and composite materials and, if possible, to mathematically model [8] the response so that expansion of any composite system consisting of the constituents may be accurately predicted. A large number of results are presented here for the expansion of the Monsanto phenolic resin SC-1008 as a function of heating rate, position within the cured block, curing treatment and repeated heating cycles. Expansion data are also reported up to 400 °C for composite systems consisting of the phenolic resin reinforced with both silica and carbon (rayon precursor) fibres. Previous publications [9, 10] have presented experimental data and numerical evaluation for the thermal conductivity of these materials from 20 to 400 °C.

2. Experimental procedure

2.1. Materials

All material and specimen preparation was carried out under the control of the UK Ministry of Defence. The expansion of the pure phenolic SC-1008 was measured after the three different curing treatments A, B and C. Details of these curing treatments are given in Table I. The resin materials all had a density of 1270 kg m^{-3}. The Monsanto recommended curing treatment [11] (material B) was found to produce an inhomogeneous, heavily cracked material which was almost useless for expansion measurements. It was thus necessary to first find a heat-treatment programme which produced a homogeneous material with an insignificant amount of porosity, and then to ascertain whether a change to the heat-treatment programme affected the expansion response. Material A was subjected to a nominal cure

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TABLE I Curing treatments for materials used in expansion tests

Material	Curing treatment
A (phenolic SC-1008)	Partial cure. Held at 80 °C for 24 h under atmospheric pressure.
B (phenolic SC-1008)	Monsanto cure. Heat to 177 °C in a large number of temperature increments from room temperature, each increment lasting up to several hours duration (atmospheric pressure).
C (phenolic SC-1008)	Hold for 24 h at 80 °C. Raise the temperature 10 °C every 24 h up to a maximum of 180 °C (atmospheric pressure).
Unidirectional silica–phenolic composite	Made by pressing together sheets of pre-preg (fibres in partially cured β-stage phenolic SC-1008) and heating to 165 °C under atmospheric pressure.
Bidirectional carbon (rayon)–phenolic composite	Heat sheets of pre-preg material to 175 °C for several hours under a pressure of 7×10^6 N m^{-2} in an autoclave.

at 80 °C for 24 h followed by substantial ageing (several days) at room temperature. Material B was cured using the complex programme recommended by Monsanto (Table I), which was found to produce the poor-quality material because of large amounts of internal cracking [12]. Material C was cured for 24 h at 80 °C, after which the temperature was raised by 10 °C to 90 °C. The resin was then cured for another 24 h. This 10 °C increment, 24-hour cycle, was repeated until the temperature reached 180 °C. This last heat-treatment programme was the nearest simulation of the Monsanto recommended programme which consistently produced uncracked phenolic resin [12].

The unidirectional silica–phenolic material consisted of the pre-preg phenolic SC-1008 reinforced with $64 \pm 3\%$ volume fraction of continuous pure fused silica fibres [9]. The composite was cured according to the curing treatment given in Table I. The resultant material possessed small elliptical pores parallel to the fibre direction. The volume fraction of pores was $3 \pm 1\%$. The material had a density of 1840 ± 30 kg m^{-3}.

The bidirectional carbon cloth–phenolic material was fabricated by stacking layers of a pre-preg eight-harness, satin weave, carbon fibre cloth woven from continuous-filament fibres made from a rayon precursor (Hitco CCA3) [9]. The composite was cured according to the curing treatment given in Table I. The volume fraction of fibres was $61 \pm 3\%$ and the volume fraction of flat elliptical pores (lying between the cloth layers) was $3 \pm 1\%$. The material had a density of 1405 ± 15 kg m^{-3}.

2.2. Expansion measurement

Thermal expansion was measured using a conventional quartz dilatometer. Specimens for the expansion measurements of the phenolic SC-1008 resin were nominally 20 mm in length with a 3 mm square cross-section. In the case of the two composite materials the specimens had a circular cross-section of 3 mm diameter. Particular care was taken when cutting specimens from a block to ensure that the ends of the specimens were parallel. All expansion measurements were carried out under a constant flow of oxygen-free nitrogen in order to prevent oxidation of the phenolic. The specimen, supported in a horizontal fused silica (quartz) tube and push-rod assembly, was inserted in a furnace capable of uniformly heating the specimen zone at various controlled heating rates from 0.1 to 20 °C. The movement of the push-rod due to specimen dilation and accompanying expansion of the quartz tube adjacent to the specimen was sensed by a linear variable differential transducer to a resolution of 1.0 μm. The output was recorded on an X–Y chart recorder. At zero electrical balance the force exerted on the specimen by the transducer spring was less than 0.7 N. Specimen temperature, monitored by a K-type thermocouple, was also recorded on the second channel of the X–Y chart recorder, thus providing a continuous record of dilation against uniform temperature increase. The thermocouple was located parallel to the mid-point of the specimen on the outside of the quartz tube (10 mm diameter), and providing the heating rate was kept below 2 °C min^{-1} the temperature lag between specimen and thermocouple was small. The accuracy and repeatability of the dilatometer on the most sensitive setting was estimated to be $\pm 2\%$ of the actual dilation and considerably better than this for most measurements.

In order to observe any further curing reactions occurring with the as-received resin, differential scanning calorimetry (DSC) up to 300 °C was carried out on a sample of the resin using a Dupont 990 thermal analysis unit with heat-flux DSC attachment.

3. Results and discussion

3.1. Phenolic resin SC-1008

In Fig. 1 expansion data are presented for a single specimen at different heating rates for a sample of material given cure C (Table 1). The response showed only slight variation over the heating range 0.5 to 3.0 °C min^{-1} and increased only at the highest heating rate of 10 °C min^{-1}. This may not have been solely a rate effect but probably was due to a non-homogeneity of temperature distribution within the poorly thermally conducting resin (0.2 to 0.3 W m^{-1} K^{-1} [10]) at higher heating rates. This was a useful observation as it suggested that, as long as the heating rate remained at or below 1.0 °C min^{-1}, a uniform temperature distribution within the resin specimen would be maintained. For this reason a standard heating rate of 0.5 °C min^{-1} was used for all subsequent tests. The specimen geometry was also chosen to ensure that a uniform temperature distribution was maintained.

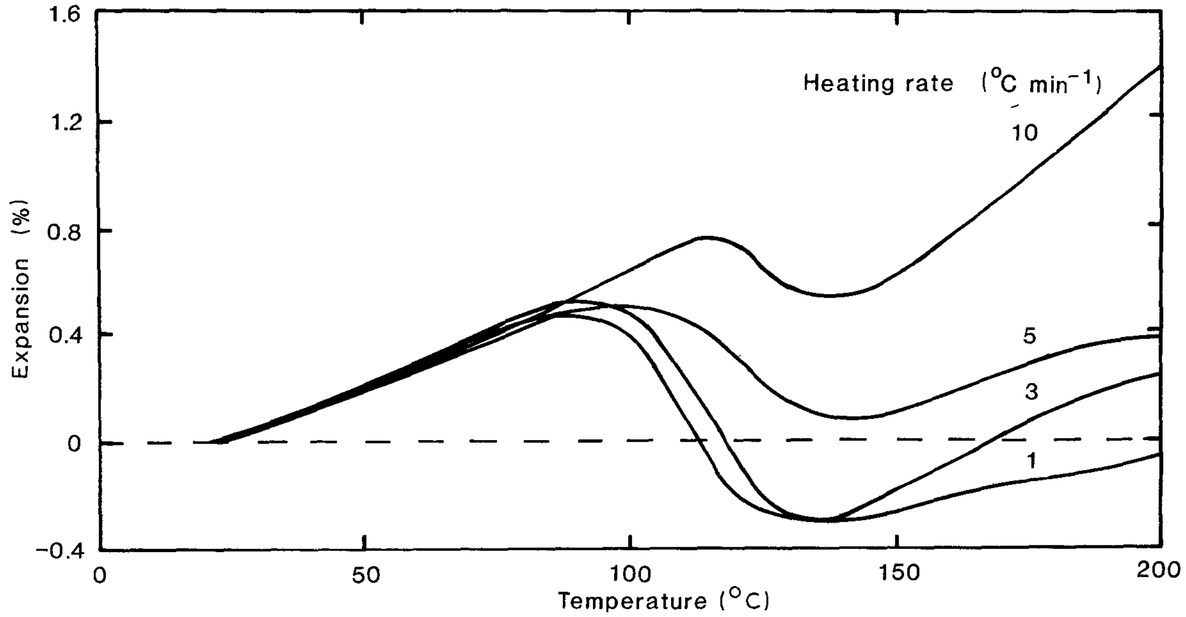

Figure 1 Effect of rate of heating on thermal expansion of phenolic SC-1008.

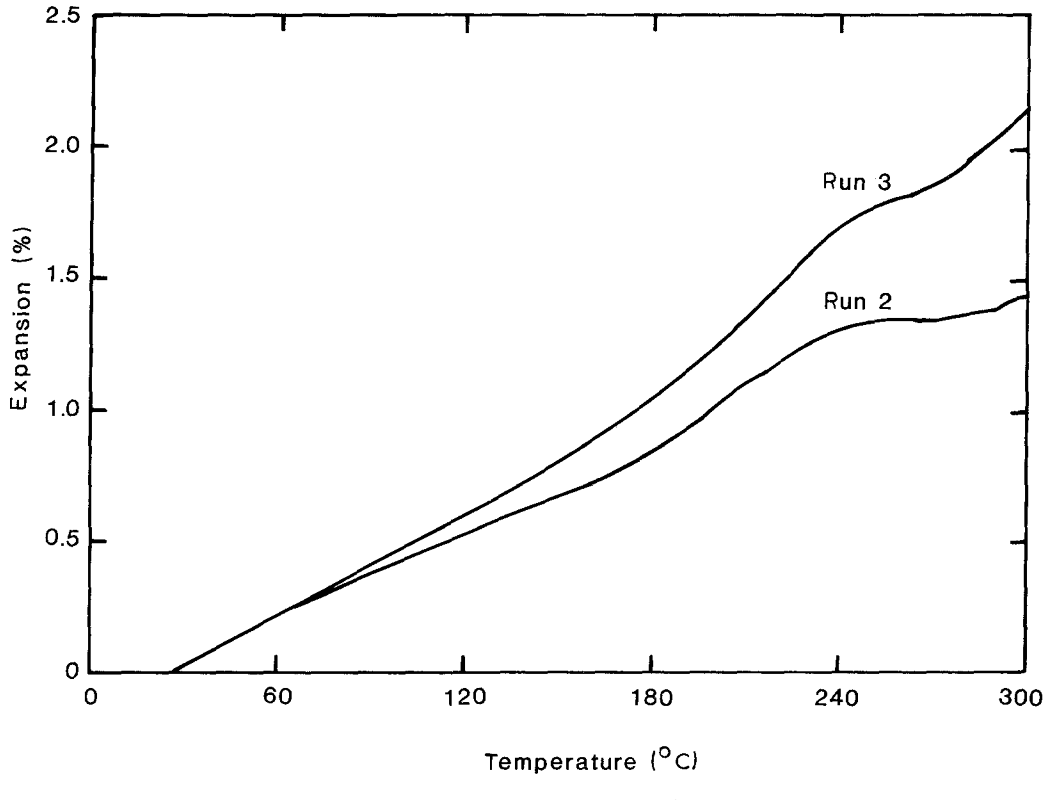

Figure 2 Thermal expansion of phenolic resin material A. Heating rate 0.5 °C min^{-1}.

The dilation measured on repeated heating cycles from room temperature to at least 200 °C (in an inert atmosphere) for materials A, B and C are presented in Figs 2 to 4. Figs. 2 shows a large specimen expansion in the second and third runs with a specimen of material A. Unfortunately, the first run was lost because of equipment failure and runs on further samples failed because of specimen distortion. The curves in Fig. 2 show a fairly linear region up to 250 °C, followed by a small plateau, and the initiation of further expansion up to the maximum temperature of 300 °C. The mean linear coefficient of thermal expansion of the phenolic resin, α, was between 49 and 70×10^{-6} °C^{-1} over most of the temperature range, with a maximum in the third run of 120×10^{-6} °C^{-1} at 221 °C.

Fig. 3 shows the expansion of material *B*, the heavily cracked phenolic SC-1008. These specimens had to be cut from the edge of the block since the central material was too heavily microcracked to yield coherent specimens. Specimen 1 gave a low expansion coefficient of approximately 20×10^{-6} °C^{-1} up to

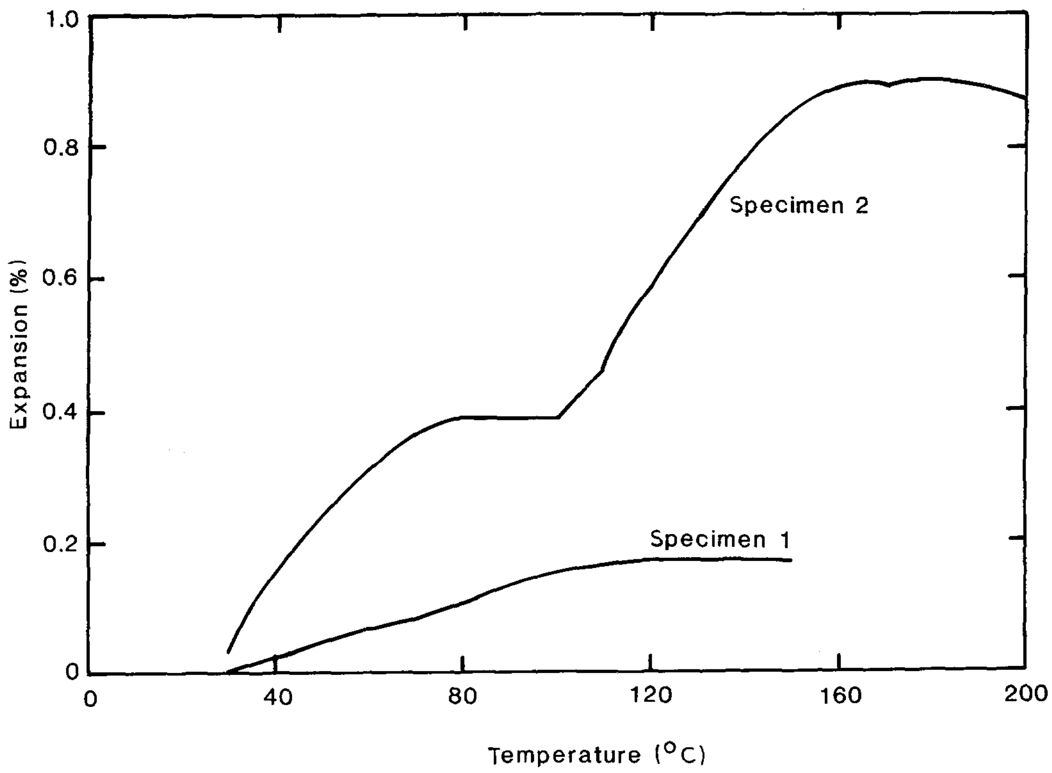

Figure 3 Thermal expansion of phenolic resin material B. Heating rate 0.5 °C min^{-1}.

80 °C, which reduced to zero when the temperature was 100 °C. Specimen 2 gave a much higher α of 80×10^{-6} °C^{-1} below 80 °C. Between 80 and 100 °C there was virtually no expansion as shown by the first plateau in Fig. 3. α then increased to 100×10^{-6} °C^{-1} after the first plateau, before again decreasing to zero at 160 °C where a second plateau was measured. Repeated measurements were not made because the material was of such poor quality that the results were not reliable. Problems were encountered in the thermal expansion measurements with material B from warping of specimens, believed to be the consequence of residual stresses (thermally induced) after curing. The presence of warping may account for the significant difference in response between the two specimens in Fig. 3.

Repeated expansion measurements up to 200 °C for material C are shown in Fig. 4. The second and third runs were almost identical, giving a mean α of 36×10^{-6} °C^{-1} over the full temperature range, considerably lower than that measured for material A. The first run for material C showed a much greater expansion than the two subsequent runs with the mean α equal to 60×10^{-6} °C^{-1} up to 100 °C. Between 100 and 120 °C, α decreased to 23×10^{-6} °C^{-1}, followed by a further increase with temperature to $> 100 \times 10^{-6}$ °C^{-1}.

It was anticipated that the semi-cured material A would have a higher α than the "fully" cured materials B and C, because the maximum curing temperature of 80 °C meant the curing was probably incomplete. The difference between the two "fully" cured materials B and C in Figs 3 and 4 may have been due entirely to the inherent variation between specimens. This observation justified the use of the material C heat-treatment for further specimens.

The first heating run for "fully" cured material always produced a different response to the subsequent runs. This has been shown in Fig. 4 for material C. The reduction in expansion coefficient between 80 and 100 °C was believed to be due entirely to loss of volatiles which caused the specimen to shrink. These volatiles have three potential sources:

(i) residues from the curing reaction (including water),

(ii) excess solvent, and

(iii) absorbed vapour species such as water (as specimens had been stored under atmospheric conditions for a period of days prior to testing).

It is suspected that, if sufficient volatiles are being driven off during an expansion test, shrinkage of the specimen can be greater than the material expansion and thus a specimen contraction is measured.

Denman [13] recorded analogous thermal expansion behaviour up to 130 °C for a similar phenolic resin CTL-91-LD. However, in his tests the resin had first been cured under an applied pressure of 7×10^{6} N m^{-2} at a maximum temperature of 177 °C for 1 h, then post-cured for several hours at 240 °C. Following the earlier observations of Pegg [14], Denman concluded that the considerable contraction (1.0%) measured in his tests (heating rate 0.833 °C min^{-1}) between 90 and 150 °C was caused by further curing and loss of residual volatiles. Denman observed no further change in specimen length when

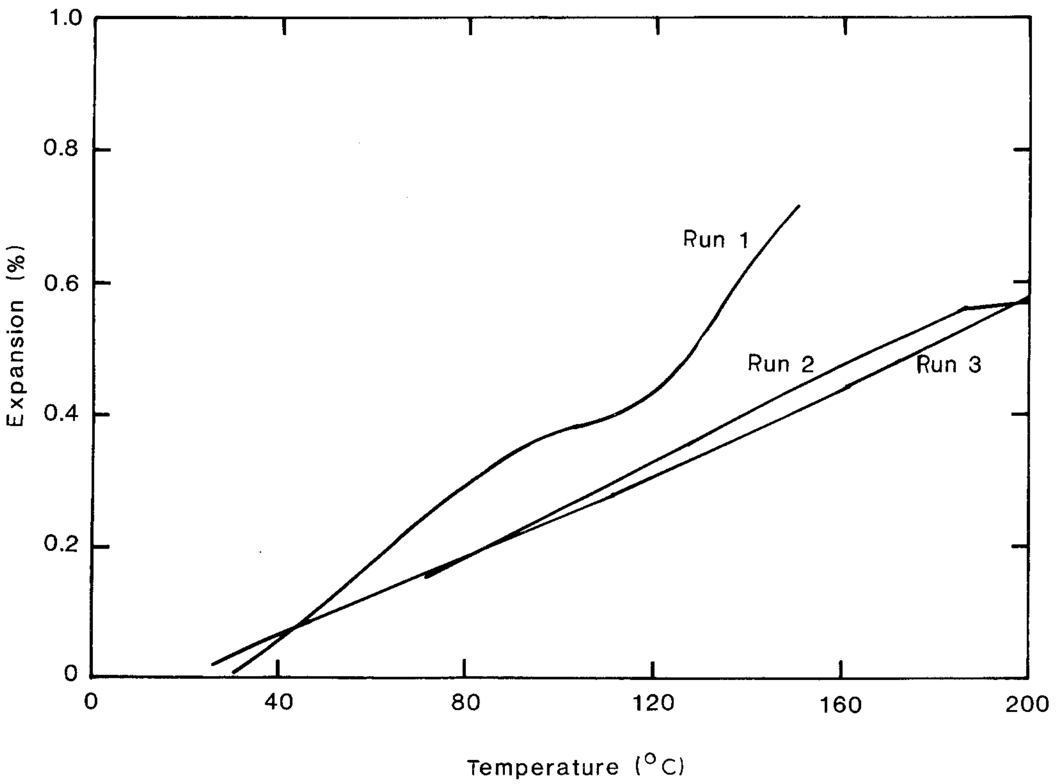

Figure 4 Thermal expansion of phenolic resin material C. Heating rate 0.5 °C min^{-1}.

the temperature increased from 150 to 200 °C. He concluded that the pressure applied during the casting process inhibited full resin cure. The phenolic resin SC-1008 used in the present work was cured under atmospheric pressure at a maximum temperature of 180 °C and a large reduction in the expansion coefficient (if not an actual contraction) was still observed. Retention of evolved formaldehyde in the curing resin may in fact help the curing process, as it is known that the formaldehyde can react with unsubstituted sites on phenol rings if it is prevented from escaping to atmosphere [15]. Therefore Denman's explanation of cure products trapped under pressure cannot fully explain the phenomenon of the observed contraction.

Fig. 5 shows the first run expansion up to 200 °C of single specimens machined at different distances from the perimeter of a cast block of material C. The cylindrical block was 25 mm thick with a diameter of 50 mm and specimens were machined at 3 mm intervals. Prior to the specimens being machined out of the block, the block had been given a prolonged soak at 180 °C. All specimens gave a similar α of between 80 and 100×10^{-6} °C^{-1} for temperatures up to 80 °C. However, above this temperature there was considerable variation in behaviour. The specimen cut 0–3 mm from the perimeter of the block contracted between 80 and 100 °C, followed by expansion at a similar rate to that measured below 80 °C. The specimen cut 24–27 mm from the perimeter also gave a definite change in expansion response above 80 °C, but in this case little contraction was detected, and thereafter α increased dramatically to a maximum of 400×10^{-6} °C^{-1}.

Apart from the anomalous behaviour of the 0–3 mm (expansion > 3–6 mm and 6–9 mm specimens) and 24–27 mm samples (expansion > 33–36 mm specimen), the other seven specimens provided expansion responses which showed a systematic increasing trend. The maximum expansion of the SC-1008 phenolic was found to change from being ~ 0.4% (specimen 3–6 mm) to ~ 1.6% (specimen 18–21 mm) as the specimen was taken from further into the block. However, the expansion response of the resin became reasonably consistent for the specimens taken from the perimeter at between 18 and 36 mm. We can only speculate as to why there was the dramatic dependency in expansion response on the location of the specimen in the block. It may have been due to a non-uniform distribution within the resin block of residual stresses near the free edge. It may have been due to a non-uniform distribution in the amount of volatile species. It may even have been due to a local variation in the chemical and physical structure of the cured phenolic. This position dependency on α was an important observation, as it suggested that the thermal expansion measurement of the pure resin was unlikely to give data relevant to the "identical" resin in a composite, where the presence of small-diameter fibres (6 to 15 µm) may affect the curing process. Unfortunately, the experimental details of monitoring specimen weight and length changes were omitted in this series of tests. Had these data been available, they might have indicated whether or not there was any positional variation in the volume of volatiles driven off during the expansion tests.

At the end of each thermal expansion run the ends

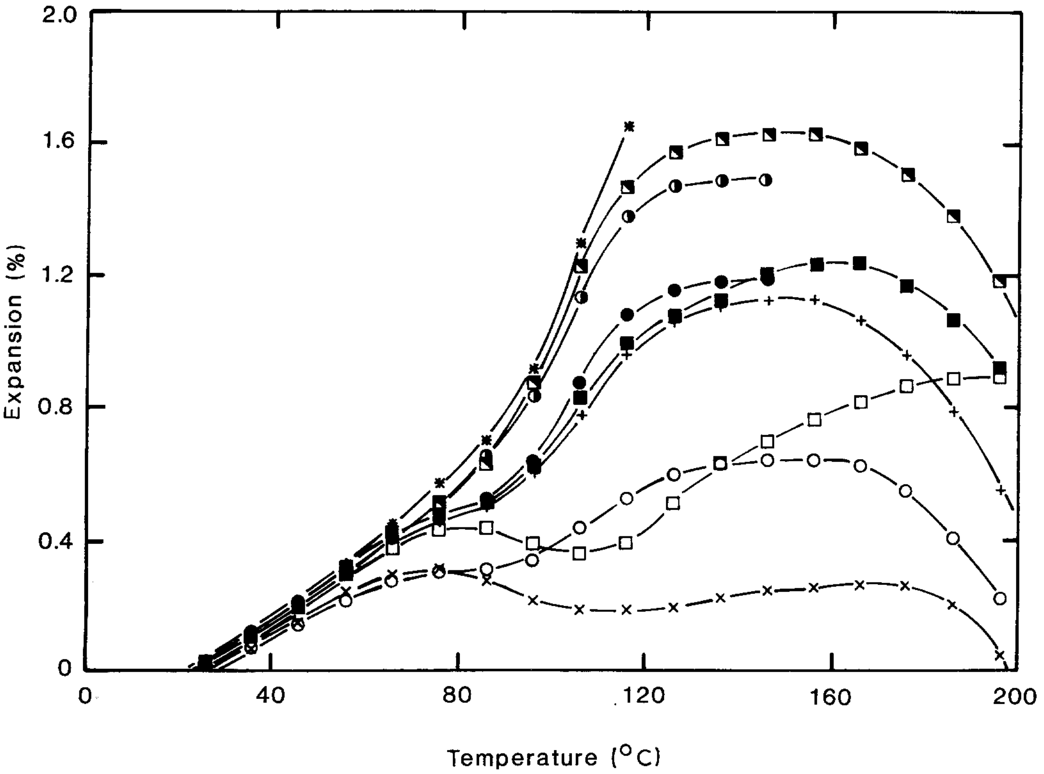

Figure 5 Thermal expansion of phenolic resin material C taken at increasing distance from the perimeter of a cylindrical block: (□) 0–3 mm, (×) 3–6 mm, (○) 6–9 mm, (■) 9–12 mm, (+) 12–15 mm, (●) 15–18 mm, (▨) 18–21 mm, (*) 24–27 mm, (◑) 33–36 mm. Heating rate 0.5 °C min^{-1}.

of the specimens were checked to see if they remained parallel. There did not seem to be detectable specimen distortion except for specimen 2 of material B (Fig. 3).

If the observed changes in expansion were due solely to the presence of solvents, absorbed volatiles (i.e. water) and volatiles (including water) evolved during the curing heat-treatment programme, annealing the specimens at a high enough temperature for sufficient time should eliminate the contraction. This has already been demonstrated in Fig. 4 where the second and third runs were similar. Since the dilation discontinuity with material C occurred between 80 and 100 °C, annealing at 100 °C may be sufficient.

Fig. 6 shows specimen percentage weight lost as a function of time. Each test at 100 °C in air was terminated after 1560 min (26 h). Comparison of the weight loss for material C with the volumes of the four specimens (Table II) showed that the greatest weight loss occurred in the lowest-volume specimen (specimen 4). This may have been due to the larger surface area per unit volume and shorter diffusion distances. The total weight loss ranged from 2.1% (specimen 1) to 3.4% (specimen 4). The results in Fig. 6 and Table II agreed with the suggestion that volatiles were trapped within the material and escaped as mobility increased at higher temperatures.

When specimens were heat-treated for 1560 min, 50% of the weight loss occurred in the first 160 min of the anneal. After this the rate of weight loss was much reduced although there was the indication of a slight increase in rate after 1200 min (20 h). This latter observation may have been the signs of the onset of secondary polymer-chemistry reaction. At the end of the 1560 min annealing process it may be reasonably assumed that the majority of the volatiles had been driven off.

Two of the above material C specimens, 1 and 4, were later heat treated at a higher temperature of 160 °C in air for a further 1650 min. The total weight loss for these two specimens is shown in Fig. 7. Surprisingly in view of the above discussion, the final total weight loss had dramatically increased on further annealing at 160 °C (9 and 12%). Yet again there was an initial rapid weight loss (half the total) followed by a lower rate and a final upturn at the end of the anneal. The result was surprising because the phenolic had already been cured at 180 °C and annealed at 100 °C; thus there should have been only a small amount of residual volatiles present with boiling points between 100 and 160 °C.

Expansion cycles to 200 °C are shown in Fig. 8 for three runs on specimen 3 (Table II) annealed for 1560 min at 100 °C (Fig. 6). A change in expansion response with each run was still apparent although the variation between runs was less pronounced. Of more interest was the temperature at which the deviation in the initial linear expansion response was noted. For the first run this now occurred at 100 °C, instead of at 80 °C with non-annealed material C (Fig. 4). The temperature at which the change was observed then increased to ~ 120 and 140 °C on the second and third runs, respectively. The initial expansion coefficient in the first run of $80 \times 10^{-6}\,°C^{-1}$ was higher than for

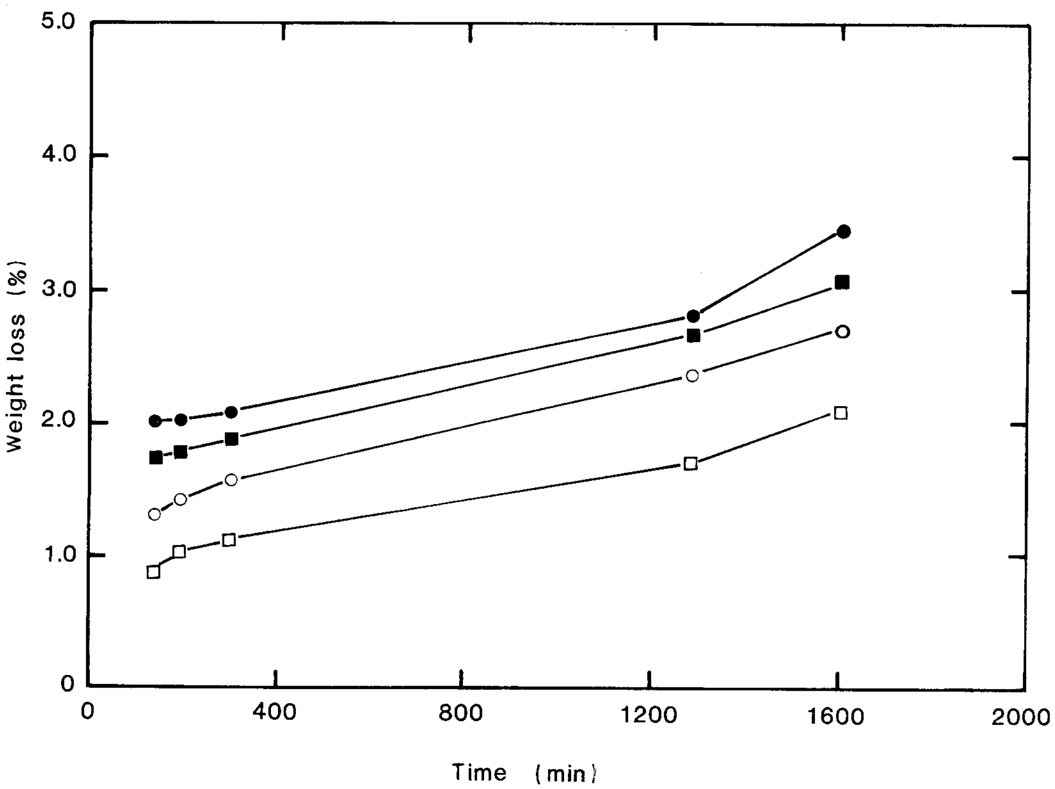

Figure 6 Weight loss of phenolic material C specimens 1 to 4 on annealing at 100 °C: (□) 1, (○) 2, (■) 3, (●) 4.

TABLE II Initial geometric properties of the annealed phenolic specimens

Specimen	Specimen dimensions (mm)			Volume (mm^3)	Surface area per unit volume (mm^{-1})
	Length	Width	Thickness		
1	20.00	3.59	3.13	224.7	1.30
2	20.22	3.11	2.68	168.5	1.49
3	20.29	3.49	1.95	138.1	1.70
4	20.23	3.07	2.18	135.4	1.67

non-annealed material. For subsequent runs α gradually reduced to give a mean of $58 \times 10^{-6}\,°C^{-1}$ up to 100 °C.

Expansion cycles are shown in Fig. 9 for specimen 4 after annealing at 100 and 160 °C (Fig. 7). The results are perhaps even more surprising, since the first run exhibited the largest contraction observed so far. The contraction occurred at a temperature above 120 °C. The contraction gradually disappeared on the subsequent two runs, with the third run giving no more than a slight discontinuity between 140 and 160 °C. The mean α up to 100 °C was $53 \times 10^{-6}\,°C^{-1}$ (Fig. 9).

The results in Figs 8 and 9 suggest that a large proportion of the anomalous behaviour of the phenolic resin can be attributed, not to the loss of pre-existing volatiles associated with residual curing products and absorbed water, but to curing products evolved during annealing or temperature cycling during the expansion measurements. The results here suggest that more curing takes place on each excursion to high temperature and the products are gradually evolved at rates which are dependent upon the mobility of the low molecular weight species within the cross-linked framework. This proposal would also account for the variation in temperature of the contraction (or decrease in expansion). Heat treatment at 100 °C will indeed drive off the volatiles (including absorbed water) which caused the contraction at 80 °C. However, this heat treatment, of relatively long time duration, also produces further curing reactions which lead to the evolution of more curing products at still higher temperatures (Figs. 8 and 9).

The curing reactions of phenolic resins in the solid state are very complicated and are not well understood [15, 16]. It also seems that, because of steric hindrance, the amount of cross-linking which occurs is much less than was once thought to be the case. Curing may continue, albeit at a reduced rate, on raising the temperature by breaking and remaking bonds in a "fully" cured material. The products so produced will include formaldehyde, water and more complicated organic products. These may be released

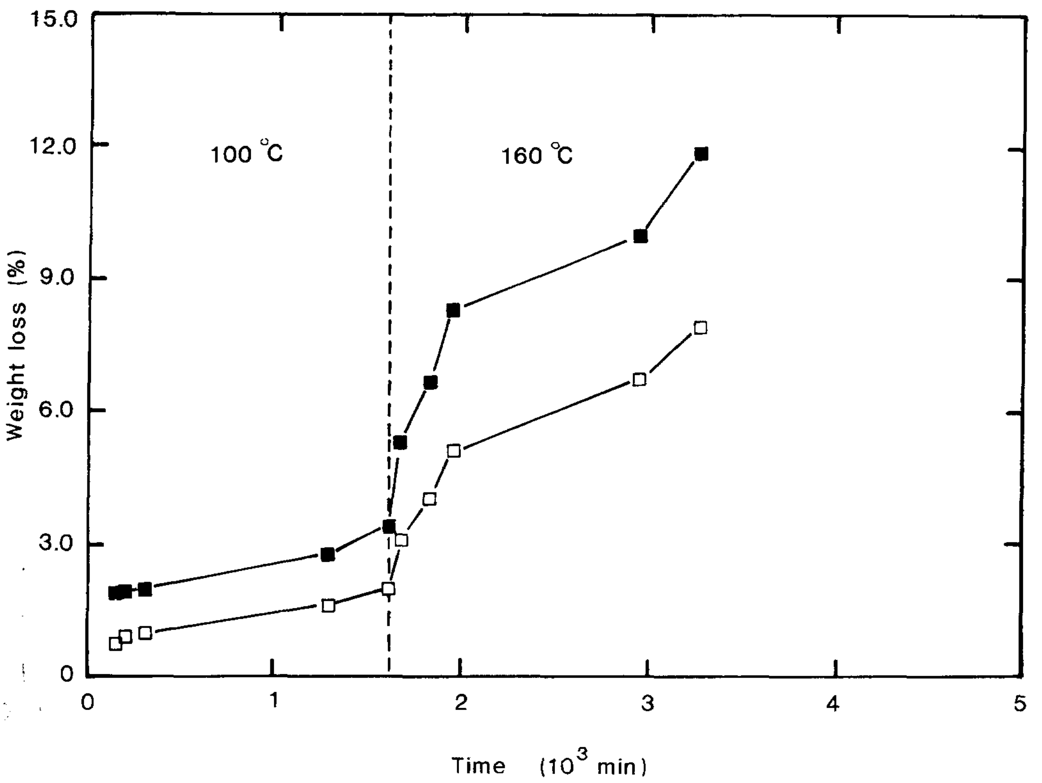

Figure 7 Weight loss of phenolic material C, (□) specimen 1 and (■) specimen 4, on annealing at 100 and 160 °C.

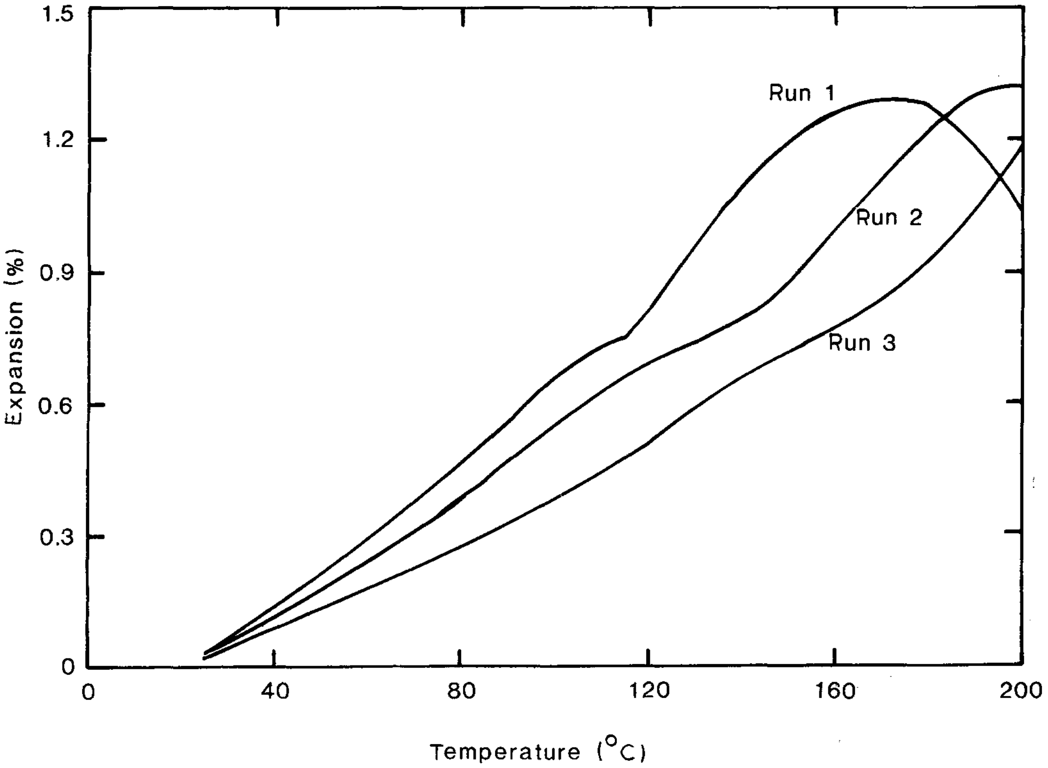

Figure 8 Thermal expansion of phenolic specimen 3 (material C) after annealing at 100 °C. Heating rate 0.5 °C min^{-1}.

in a wide range of temperatures from 50 to 200 °C.

DSC was used with as-received material C to try and evaluate the reactions occurring. The atmosphere surrounding the sample was air which provided oxygen for oxidation of the phenolic. The heating rate of 20 °C min^{-1} was much higher than in the expansion tests. The DSC curve in Fig. 10 shows an endotherm between 20 and 150 °C associated with loss of volatiles. At 150 °C an exothermic reaction began and gradually increased in intensity due to preliminary oxidation of the phenolic resin. The translucent amber resin darkened due to the oxidation process when the

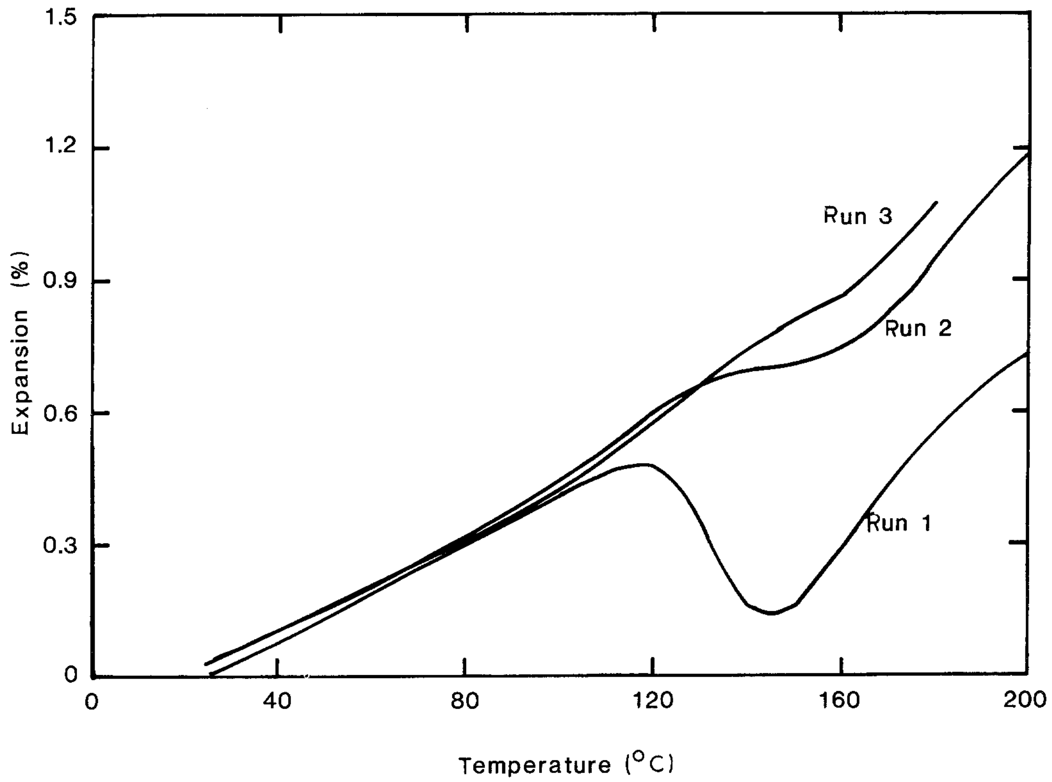

Figure 9 Thermal expansion of phenolic specimen 4 (material C) after annealing at 100 and 160 °C. Heating rate 0.5 °C min^{-1}.

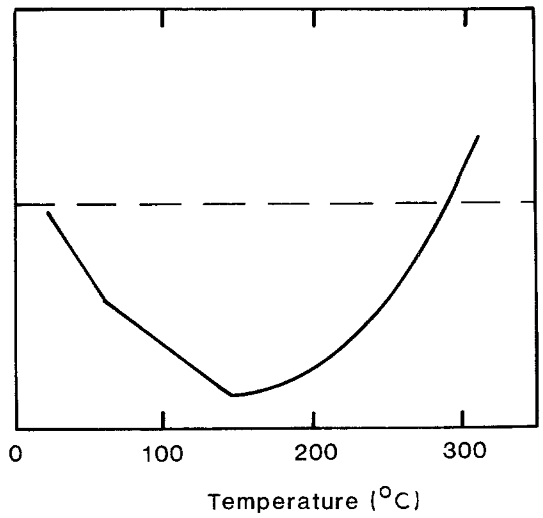

Figure 10 Differential scanning calorimetry of material C phenolic SC-1008. 20 °C min^{-1} in air; reference is glass beads.

temperature exceeded 210 °C. It was also possible that some of the energy for the exotherm came from the resin continuing to cure.

We thus have conflicting evidence which suggested on the one hand that the expansion response of SC-1008 was due to absorbed and residual curing volatiles, and on the other hand to further curing reactions which evolved volatile species. The time duration used in the annealing treatments was four times the time duration during an expansion test, when the heating rate was 0.5 °C min^{-1}. The former annealing may have allowed slower curing reactions to continue for extended periods. This may have led to a build-up in the volatiles (to be driven off at a higher temperature) to an extent which was not encountered in the shorter time duration of the expansion testing. Thus in the absence of this build-up in curing products, the absorbed volatiles (principally water from the atmosphere) played the dominant role.

What the expansion data also demonstrated very noticeably was the large variation in the thermal expansion of phenolic SC-1008 taken from different areas within the same cast block. This is believed to occur because

(a) the rate of volatile diffusion and the soak time at the maximum curing temperature were not sufficient to produce total resin stability, and

(b) the rate of volatile absorption from the atmosphere gave an absorbed volatile concentration gradient across the block, with the highest concentration near the free edges.

Additionally, cooling down from the maximum curing temperature produced internal stress fields in the resin which are believed to affect the body more than the surface of the block as illustrated by the severe cracking in material B. It therefore remains extremely difficult to quote typical thermal expansion data for the phenolic SC-1008.

It is also of interest to observe that after the material C resin had been heated to 200 °C it stabilized so that the contraction at 80 °C disappeared entirely and the expansion behaviour was reproducible on repeated heat cycles (Fig. 4). This behaviour was presumably the result of all volatile species being driven off and all curing reactions being completed. For design purposes a mean linear coefficient of thermal expansion in the range $(55 \pm 5) \times 10^{-6}\,°C^{-1}$ up to 100 °C (Figs 8 and 9) may be acceptable for phenolic SC-1008 which

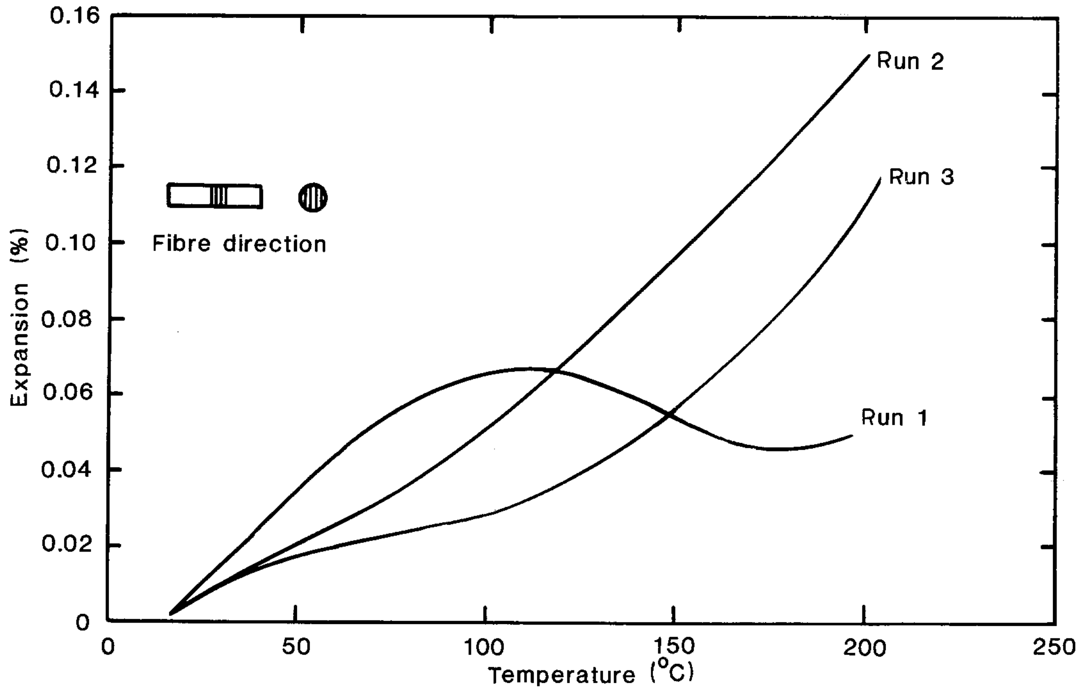

Figure 11 Thermal expansion transverse to fibre orientation of a unidirectional silica–phenolic composite. Heating rate 1.0 °C min^{-1}.

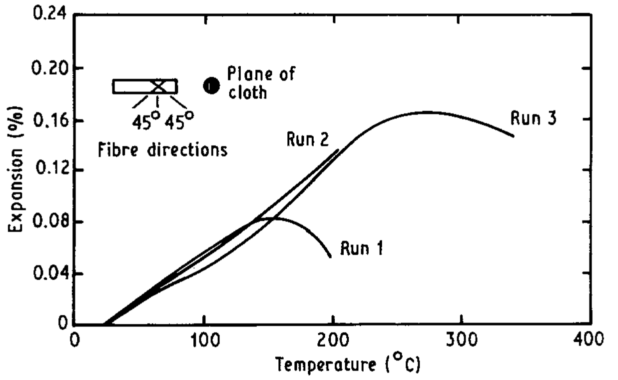

Figure 12 Thermal expansion of a bidirectional carbon–phenolic composite. Heating rate 1.0 °C min^{-1}.

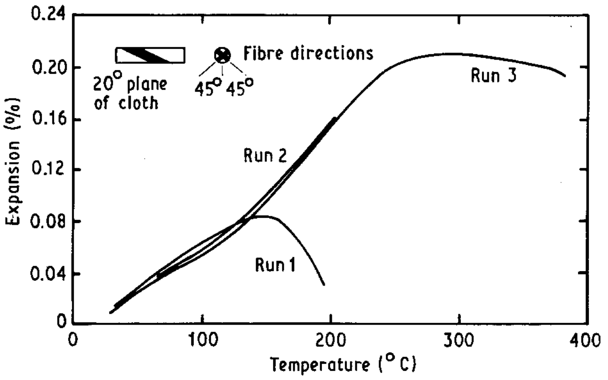

Figure 13 Thermal expansion of a bidirectional carbon–phenolic composite. Heating rate 1.0 °C min^{-1}.

has been heat-treated at a high enough temperature (> 200 °C) to stabilize the resin.

3.2. Fibre–phenolic composite systems

Figs 11 to 13 present typical expansion data recorded for composite systems in those directions where the expansion of the resin was expected to dominate. Although the heating rate in these tests was raised to 1.0 °C min^{-1}, a uniform heating rate was still maintained as both the silica and carbon fibre used have higher thermal conductivities [10] (silica fibres 1.2 to 2.0 W m^{-1} K^{-1} and carbon fibres 2.0 to 3.0 W m^{-1} K^{-1} (along length) than the phenolic SC-1008 (0.2 to 0.3 W m^{-1} K^{-1}). It was standard practice to anneal the composite specimens at 200 °C before the thermal expansion measurements. For the measurement directions chosen the composites showed a similar behaviour to the pure resin (Figs 1 to 4), in that the expansion response was different on the first run and became more consistent on subsequent runs. The similar expansion response confirmed the expectation that the resin dominated the expansion in the directions measured. The temperature rise before a contraction was observed was now higher for both composite systems than for the resin (~ 100 °C for the silica–phenolic (Fig. 11) and ~ 150 °C for the carbon–phenolic (Figs 12 and 13)). The maximum expansions for the composites were much less than for pure resin, not an unexpected result since both fibres have coefficients of expansion below 5×10^{-6} °C^{-1} (cf. phenolic SC-1008, α in the range 40 to 60 $\times 10^{-6}$ °C^{-1}). For the unidirectional silica–phenolic material the maximum thermal expansion transverse to the continuous fibres was 0.15% at 200 °C. For the carbon–phenolic cloth material the two measurement directions in Figs 12 and 13 gave maximum expansions of 0.17 and 0.21% at ~ 250 °C. These maximum expansions compare with a total expansion of 0.58% for phenolic SC-1008 (material C, Fig. 4) at 200 °C. Thus the presence of fibres at a volume fraction of 60 + % had reduced the thermal expansion to < 1/3 that of the pure resin. Due to the unresolved difficulties in obtaining reliable and relevant measurement of the coefficient of thermal expansion for the phenolic resin and other properties such as moduli, it has not been possible with the data presented here to apply micromechanical modelling techniques [8] to predict the transverse expansion coefficient for the reinforcing fibres.

As was found with the thermal expansion of the bulk resin (Figs 1 to 4), thermal history had a profound effect on the expansion of the composites during repeated heating cycles (Figs 11 to 13). With respect to the composite expansion other factors, as well as those already discussed with respect to the expansion of the resin, were known to be involved. The curing treatments for the composites material are given in Table I. Based on our experience with the resin, the differences in heat treatment between the material C phenolic and composites is one likely reason why there was a difference between the first-run expansion response of the composites (Figs 11 to 13) and the resin (Fig. 4). Additional reasons will now be discussed. Both fibre composite systems contained residual stresses at room temperature (20 °C), generated when the materials were finally cooled down from the maximum curing temperature. These residual stresses were a result of the large mismatch in coefficients of thermal expansion between fibres and resin. Although the internal stresses were largest parallel to the continuous fibres, Poisson's ratio effects would have ensured that residual stresses also acted in the direction perpendicular to the fibres.

On heating during a thermal expansion test, the residual tensile stresses in the matrix were reduced and finally completely relieved. There should have existed a temperature range over which the average thermally induced stresses were nominally zero. If the residual stresses were such that the tensile strength of the resin had not been exceeded, the zero-stress temperature should have coincided with the curing temperature for the composite. As the composite was heated through the maximum curing temperature on the first run, the expansion response may have been affected by an inversion of stresses. That is, below the curing temperature the fibres were in axial compression and above they were in tension. The reversal in stresses may be expected to have occurred over a fairly large temperature range since the interfacial bond between the fibres and resin would not have been constant.

During the first run, the temperature associated with the start of the contraction was 65 °C below the curing temperature of 165 °C for the silica–phenolic material (Fig. 11), and 25 °C below the curing temperature of 175 °C for the carbon–phenolic material (Figs 12 and 13). The recorded anomalies between bulk phenolic and the two composite systems on the first heating cycle may have been due to a combination of the redistribution of thermally induced stresses and resin shrinkage due to loss of volatiles. It should be remembered that the different curing treatments for the composites and resin (Table I) would have yielded initial-state resin that was non-consistent. In the case of the carbon cloth–phenolic composite there would have been further shrinkage of the resin during heating since pressure was applied during the casting [13], entrapping more of the curing volatiles. To a lesser extent the additional physical properties, i.e. of the resin being finely dispersed between fibres; of a small percentage volume fraction of voids (< 4%) being present; and of a potential microcrack network in the composites, may all have contributed to the different expansion response. Closure of the microcrack network during heating may have provided a compensating mechanism for the composite expansion.

The composite thermal expansion response was found to be dependent on the combination of several factors, all of which can vary from specimen to specimen. Therefore, the problem of establishing relevant thermal expansion data from the first heating cycle measurements was found to be more acute than had already been established for the bulk phenolic SC-1008. This conclusion from the results given here increases the already daunting task faced by design engineers in choosing reliable and relevant thermal expansion design data from the available sources [17].

Annealing the composite systems at 200 °C not only removed all the volatiles, but appeared to have relieved the residual stresses. Thus, on subsequent heating runs the thermal expansion behaviour of the composites up to 200 °C was closer to that observed for the stabilized bulk resin (cf. run 2 in Fig. 4 and run 2 in Figs 11 to 13), although the difference in absolute expansion is approximately a factor of four.

4. Conclusions

1. Thermal history has a profound effect upon the thermal expansion response of the phenolic SC-1008 and its composites.

2. Resin softening, providing specimen distortion when the temperature exceeds 200 °C, limits measurement of thermal expansion of the pure phenolic to 200 °C.

3. Residual stresses and volatiles, from resin curing and absorbed water, cause a large variation in the thermal expansion response, particularly on the first heating cycle. Annealing the cured resin materials at 100 and 160 °C for prolonged periods of time in an attempt to drive off the volatiles is found inappropriate because (a) secondary curing reactions activated by prolonged annealing produce more volatiles, and (b) storage of the materials in atmospheric conditions allows absorption of moisture and other volatile species.

4. Non-uniform distributions of volatiles and residual stresses cause variations in thermal expansion response throughout a single block of pure resin.

5. The bulk phenolic resin thermal expansion may not be the same as the resin expansion in the two composites. This poses an unresolved problem when evaluating thermal expansion measurements in an attempt to obtain the constituent coefficients of thermal expansion for design purposes.

6. The results presented in the paper suggest that in future a consistent phenolic material would be obtained by curing at a much higher temperature, say 250 °C (atmospheric pressure), than the temperatures

currently used in the composite manufacture (maximum 175 °C, see Table I). Application of the current curing treatments gives a large variation in the expansion response which is indeterminate.

7. The linear coefficient of thermal expansion for the phenolic SC-1008 up to 100 °C, which has been stabilized at a high enough temperature (> 200 °C), is in the range $(55 \pm 5) \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$.

8. The presence of either continuous unidirectional silica or bidirectional (cloth) carbon (rayon precursor) fibres at a volume fraction of ~ 60% reduces the composite thermal expansion, in those directions where the resin dominates to < 1/3 that of the pure phenolic.

Acknowledgement
This work has been carried out with support of Procurement Executive, Ministry of Defence. The authors would like to acknowledge the supply of material and helpful discussions with Dr B. Derry and Mr E. Gunn of the MoD.

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Received 20 May
and accepted 26 September 1991