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Flexural mechanical properties of thermally treated unidirectional and cross-ply Nicalon-reinforced calcium aluminosilicate composites

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Long, square cross-section samples of a unidirectional and a cross-ply $[0/90]_{3s}$ silicon carbide (Nicalon) fibre calcium aluminosilicate glass-ceramic matrix composite have been subjected to a range of thermal treatments. They were held at temperatures up to 800 °C above room temperature for 1, 6 or 24 h then slowly cooled or quenched into water. The thermal cycle was repeated up to six times for a small number of samples. The effects of these thermal regimes on Young's modulus, onset of matrix cracking (as assessed by onset of non-linearity in the load–displacement curve) and flexure strength have been monitored using three-point flexure testing. In very broad terms, where clear trends emerged, the intermediate temperature differentials, i.e. 400–650 °C, have been found to have the most detrimental effects on properties, and this has been linked to expected changes in the carboneous interphase and its subsequent replacement by silica.

1. Introduction

Ceramic matrix composite materials are expected to be used in high-temperature environments and will be subjected to both thermal and mechanical stresses, hence an understanding of the effect of thermal treatment on retained mechanical properties is of great importance. Matrix cracking due to mechanical loading in continuous fibre-reinforced systems has been well documented, (e.g. [1–4]). There is, however, a lack of literature pertaining not only to matrix cracking under thermal shock conditions but also to the effect of thermal treatments on the behaviour of materials under subsequent mechanical loading. Experiments which produce matrix cracking as a result of a thermal shock have been performed on unidirectional and cross-ply silicon carbide fibre-reinforced calcium aluminosilicate [5, 6], unidirectional silicon carbide fibre-reinforced magnesium aluminosilicate [7], and on unidirectional Nicalon fibre-reinforced borosilicate glass and lithium aluminosilicate (LAS) composites [8]. Thermal shock resistance of cross-ply ceramic matrix composites has been considered in a theoretical study [9].

An important result from previous experimental work is the nature of the damage patterns, specifically matrix cracking, introduced into composites as a result of thermal shock, because these damage patterns may affect the stiffness of the composite and may grow under any subsequent loading. In cuboid samples of unidirectional SiC/CAS, two types of matrix cracking were seen [5]. On the end faces of the samples (i.e. on planes that were perpendicular to the fibre direction), major cracks were seen in the region of the mid-plane of the laminate; these cracks were oriented parallel to the mid-plane of the laminate and penetrated some distance into the sample, the distance depending on the temperature difference of the thermal shock. On the side faces of the samples (i.e. on planes parallel to the fibre direction), an array of matrix cracks were seen, oriented perpendicular to the fibre direction, similar to the classic matrix crack pattern seen in a unidirectional composite subjected to mechanical loading. The average spacing (i.e. density) of these cracks depended on the severity of the shock. In cross-ply laminates [6], the matrix cracking was mainly in the plies towards the centre of the laminate and the damage within individual plies was similar to that seen in the unidirectional laminates, i.e. on the faces of the sample to which the fibres in a particular ply were perpendicular major cracks were seen oriented parallel to the mid-plane of the laminate, while on the faces of the sample to which the fibres in a particular ply were parallel an array of matrix cracks was seen, oriented perpendicular to the fibre direction.

To assess the effect of thermal treatments on residual mechanical properties, an appropriate test method has to be chosen. Flexure testing is one of the preferred techniques for determining mechanical properties, due

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mainly to relatively simple fixture and specimen geometries, although several research groups [10–12] have stressed that precautions must be taken to ensure valid testing conditions when using this method. This study employs a three-point bend test method in order to assess the mechanical behaviour of unidirectional and cross-ply continuous silicon carbide (SiC) fibre-reinforced calcium aluminosilicate (CAS) matrix composites after samples have been subjected to various thermal regimes.

2. Experimental procedure

2.1. Specimen lay-ups and sample size

The material used in this study was a calcium aluminosilicate matrix reinforced with tows of silicon carbide fibres (Nicalon). Two configurations were used for the experimental programme: a unidirectionally reinforced composite of twelve plies ($[0]_{12}$), each approximately 180 μm thick, and a cross-ply ($[0/90]_{3s}$), both supplied by Rolls-Royce plc.

In this study the depth of sample was restricted by the thickness of the plates to 2.3 mm so that the suggested minimum span in three-point bending necessary to produce a tensile failure is 46 mm [13]. Earlier work [5] had indicated that cracks introduced on the end faces of unidirectional samples as a result of thermal shock may penetrate up to 5 mm into the ends of the sample. Hence the length of the bend test samples was approximately 20 mm longer than the span, i.e. 66 mm long, in order to eliminate any effects due to these cracks. The widths of the unidirectional samples were approximately equal to the depths (2.3 mm) in order to maintain a square cross-section (as used for other experiments) and fibres were oriented parallel to the long dimension of the bar. The width of cross-ply samples was 5 mm in order to try to minimize any effect of oxygen piped down the interface of the transverse plies during thermal aging, whilst still attempting to retain a small cross-section. After cutting samples from the plates using a high-speed diamond saw, the matrix-rich coating on the tensile surface of the samples was removed by polishing to improve subsequent detection of cracking damage by reflected light microscopy (RLM) and to present a flat face to the loading rollers of the test rig. The side and tensile surfaces of all samples were prepared to a high standard finish.

2.2. Thermal treatments

Samples of the dimensions given above were thermally treated to give temperature differentials between 200 and 800 °C and ageing times of 1, 6 or 24 h before being rapidly quenched in water or slowly cooled. Some of the samples were subjected to multiple thermal shocks, i.e. thermal ageing and quenching were repeated several times prior to mechanical testing.

2.3. Flexure testing

A series of three-point flexure tests were conducted in order to obtain values of Young's modulus, onset of non-linearity and flexure strength. From beam theory, the Young's modulus for the composite can be calculated using the relationship

$$E = \frac{WL^3}{48I} \tag{1}$$

The slope of the initial linear section of the load–displacement curve, W/δ, may be obtained by measuring the displacement, δ, immediately opposite the central loading point for a given load, W. W may be obtained directly; the value of δ, however, must be corrected by subtracting the deflection due to the inherent stiffness of the machine/fixture. This was achieved by "bending" a rigid sample in the fixture and measuring the apparent deflections at given applied loads. L is the span of the beam and I is the second moment of area.

The onset of matrix cracking in undamaged material or the development of further cracking in damaged material is associated with the onset of non-linearity in the load–displacement curve, i.e. the point of deviation from an initial straight line. Corresponding stress values can be calculated using the standard three-point bending relationship

$$\sigma_b = \frac{3WL}{2bd^2} \tag{2}$$

where b and d are the breadth and depth of the sample, respectively.

If the beam is assumed to behave in a linear elastic manner up to fracture, then the maximum tensile stress that the material can support is given by Equation 2 where W is the maximum load. It is recognized that the materials do not behave elastically in this way – the maximum stress is used as a comparative indicator of behaviour.

Treated and as-received samples were tested in the three-point bend test mode from which load–displacement curves were produced. The sequence of cracking damage with progressive increase in applied flexure loading was observed by loading the sample to produce cracks, removing the load, viewing the surface by RLM and recording the crack pattern before repeating the procedure for greater loads.

3. Results

3.1. Unidirectional Nicalon-reinforced CAS

3.1.1. Young's modulus

Results from slow-cooling and single thermal shock (i.e. water quench) experiments were obtained from three-point flexure tests using Equation 1 and are summarized in Fig. 1; also included is the mean of six results from tests on samples of as-received material.

The value of Young's modulus calculated from the load–displacement curve for all slowly cooled samples was 120 ± 6 GPa. For thermally shocked samples, Young's modulus values were reduced. The greatest effect was at 650 °C, where the value was reduced to less than 100 GPa after only 1 h heat treatment. Samples exposed to a thermal ageing temperature of 800 °C, for shorter duration heat treatments show an

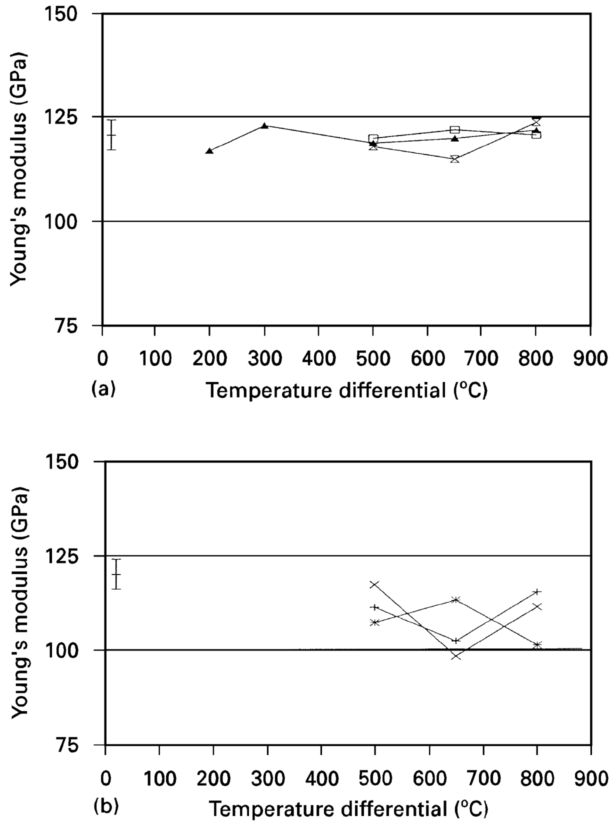

Figure 1 Young's modulus of thermally treated unidirectional Nicalon/CAS: (a) slowly cooled (□) 1 h, (▲) 6 h, (■) 24 h; (b) water-quenched (×) 9 h, (+) 6 h, (*) 24 h.

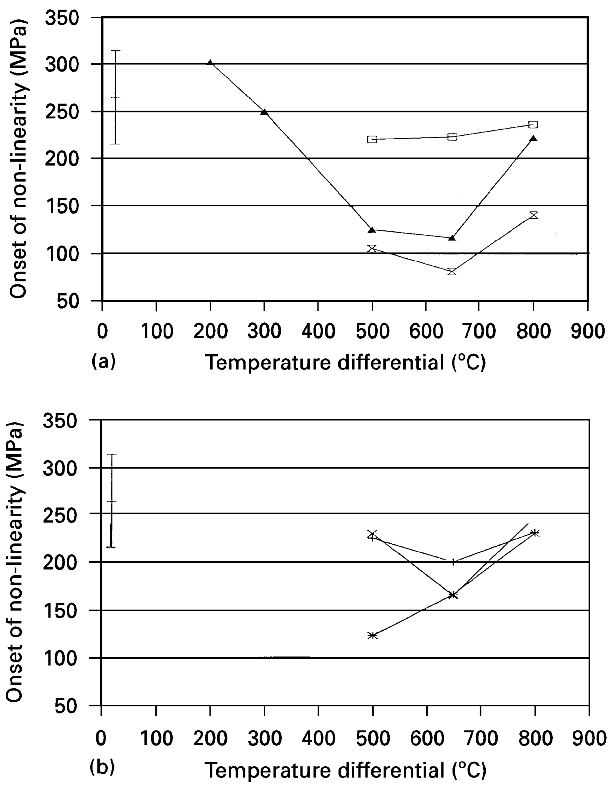

Figure 3 Onset of non-linear behaviour of thermally treated unidirectional Nicalon/CAS: (a) slowly cooled (□) 1 h, (▲) 6 h, (■) 24 h; (b) water quenched (×) 1 h, (+) 6 h, (*) 24 h.

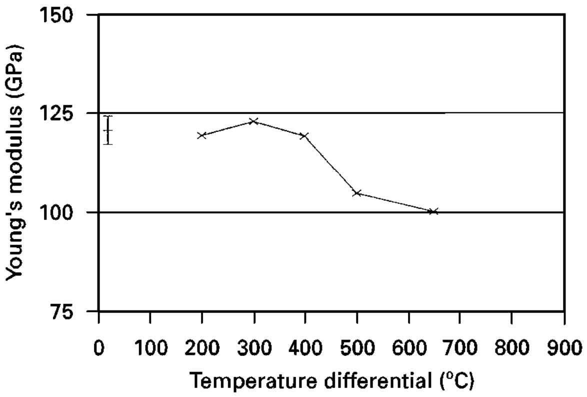

Figure 2 Young's modulus of a unidirectional Nicalon/CAS after six cycles of thermal ageing for 1 h and quenching.

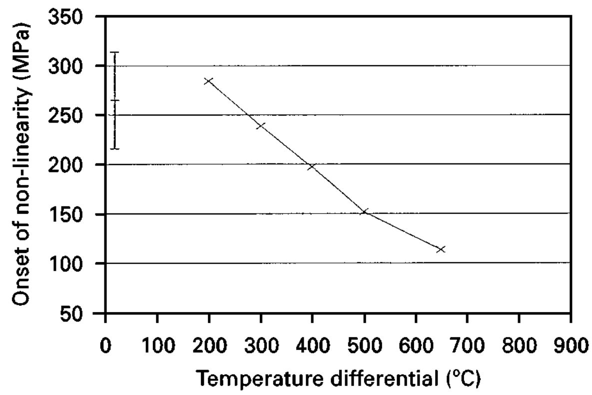

Figure 4 Onset of non-linear behaviour of unidirectional Nicalon/CAS after six cycles of thermal ageing for 1 h and quenching.

increase in modulus compared to those aged at 650 °C. The results for Young's modulus following multiple thermal shock cycles (Fig. 2) indicated a definite trend of a reducing modulus with increasing severity of thermal treatment above 400 °C.

3.1.2. Onset of non-linearity

The stress values at the onset of non-linearity in the load/displacement curve are shown in Fig. 3 for single thermal cycles and in Fig. 4 for multiple thermal shocks. These stress values correspond to the initiation of matrix cracking in undamaged samples or the development of further damage in samples cracked as a result of prior thermal treatment. The stress level at the onset of non-linear behaviour appeared to be unaffected by low temperature ($< 500\,^{\circ}C$) thermal ageing. Samples exposed to higher temperatures for short duration did not appear to have been affected significantly either, but extending thermal ageing times resulted in a reduced ability to sustain loads without the occurrence of matrix cracks. For example, thermal ageing at 650 °C for 1 h required a composite flexure stress of 223 MPa to cause non-linear behaviour compared with 117 MPa after 6 h and 81 MPa after 24 h. An improved resistance to matrix cracking especially at the longer ageing times was observed when the ageing temperature was increased to 800 °C. The behaviour of samples thermally shocked after the completion of the ageing stage appeared to indicate a similar trend to that of the slowly cooled samples.

The effect of multiple thermal shocks on the composite was most pronounced at a temperature differential of 650 °C where the effect was seen as a reduction in stress level from 265 MPa for as-received material to only 114 MPa after six thermal cycles.

3.1.3. *Flexure strength*

Flexure stress values are shown graphically in Figs 5 and 6. For most thermal ageing regimes the flexure strength remained within the scatter band of the values obtained for the as-received unidirectional material. The effect of thermally shocking the samples was, if anything, to reduce the flexure strength, from the slowly cooled values, by a small amount, e.g. 924 MPa for samples slowly cooled after ageing for 24 h at 500 °C, but 860 MPa when subjected to a single thermal shock. The deterioration in flexure strength capabilities for multiple thermal shocks above 400 °C is also shown clearly in Fig. 6.

3.2. $[0/90]_{3s}$ cross-ply Nicalon-reinforced CAS

3.2.1. *General comments*

Results were obtained from three-point flexure tests for as-received samples of the cross-ply composite in a similar manner to that described in Section 3.1 for the unidirectional material. The sequence of cracking features which developed under mechanical load was recorded and is shown schematically in Fig. 7. An example of the crack pattern on a side face at peak stress is shown in Fig. 8.

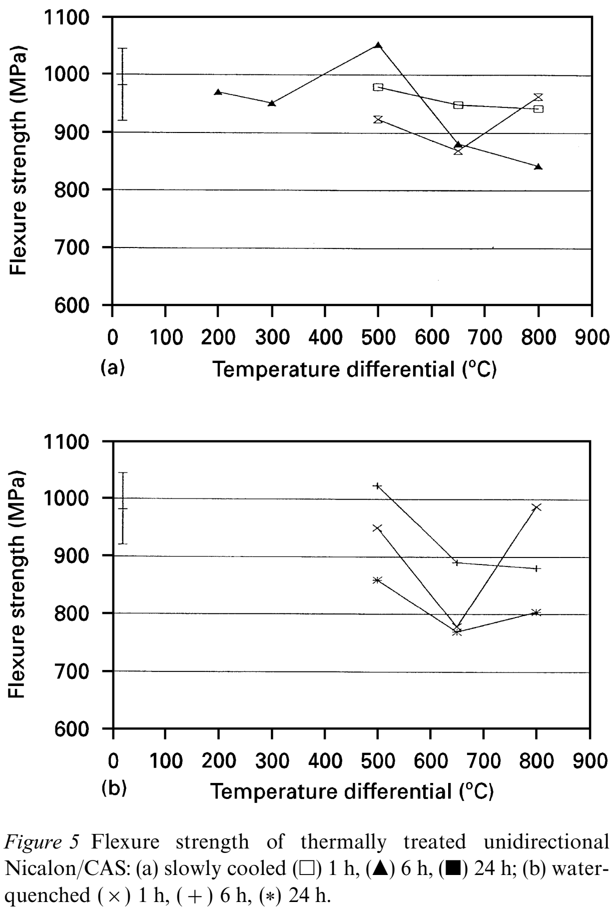

Figure 5 Flexure strength of thermally treated unidirectional Nicalon/CAS: (a) slowly cooled (□) 1 h, (▲) 6 h, (■) 24 h; (b) water-quenched (×) 1 h, (+) 6 h, (∗) 24 h.

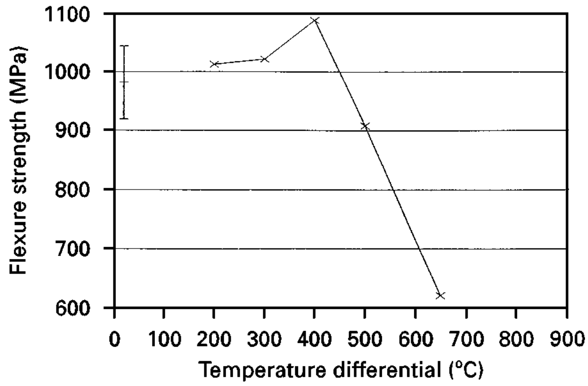

Figure 6 Flexure strength of unidirectional Nicalon/CAS after six cycles of thermal ageing for 1 h and quenching.

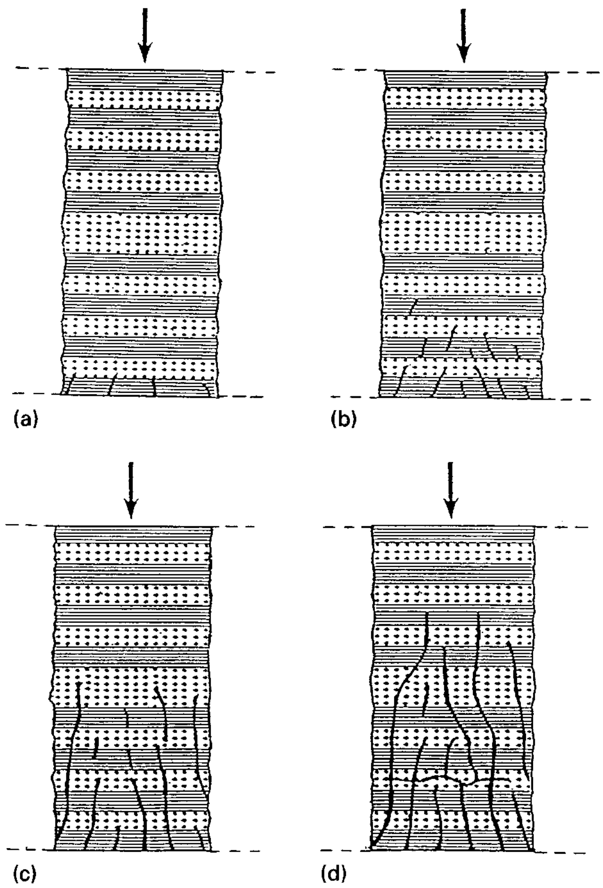

Figure 7 Schematic representation of the sequence of cracking events in $[0/90]_{3s}$ Nicalon/CAS subjected to three-point bending.

3.2.2. *Young's modulus*

The values obtained for the Young's modulus of the cross-ply material (Fig. 9) appeared to indicate a trend of a modulus reduction (from the as-received value) with increasing severity of thermal shock. The effect of the multiple quenching regime was to amplify this effect by decreasing the temperature differential at which a reduction in modulus became apparent.

3.2.3. *Onset of non-linearity*

There appeared to be little modification to the level of stress at the onset of non-linear behaviour for all thermally shocked samples (Fig. 10) because only

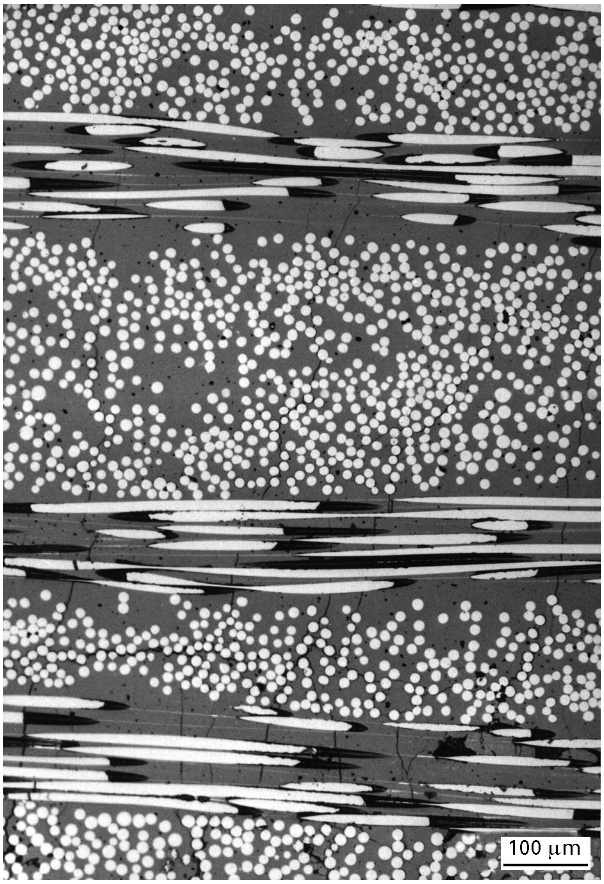

Figure 8 Reflected light photomicrograph of $[0/90]_{3s}$ Nicalon/CAS showing crack distribution at peak stress.

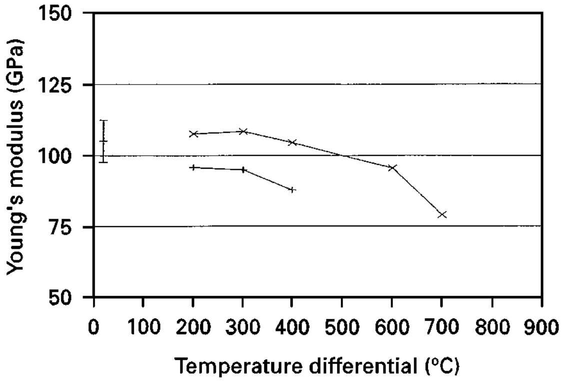

Figure 9 Young's modulus of thermally treated $[0/90]_{3s}$ Nicalon/CAS: (×) 1 h, (+) 6 × 1 h quenching.

those samples aged for 1 h at 600 or 700 °C exhibited non-linear behaviour at applied composite stresses below 100 MPa.

3.2.4. Flexure strength

The results for the flexure strength of the as-received cross-ply composite are shown in Fig. 11. The trends of these data have some similarities with the trend in Young's modulus, although the only real change outside the experimental variation may be to samples quenched after thermal ageing for 1 h at 600 or 700 °C.

4. Discussion

4.1. Unidirectional Nicalon-reinforced CAS

4.1.1. Young's modulus

The measurement of Young's modulus is a useful indication of the initial integrity of the composite, in particular the matrix and interfacial properties. The experimental value of Young's modulus for the as-received unidirectional Nicalon/CAS of 120 $\pm$ 6 GPa was in close agreement with the value of 124 GPa obtained from the rule of mixtures method (using the values of $E_f = 190$ GPa, $E_m = 90$ GPa, and $V_f = 0.34$) and values obtained from uniaxial tensile tests [14, 15]. These results suggest that the use of simple rule-of-mixtures calculations on flexure test data is valid for undamaged material.

The values of Young's modulus calculated from the series of thermally aged and slowly cooled experiments were similar to the as-received values which suggests that there was no detectable damage to the matrix of the material over the range of ageing times and temperatures used in this study.

Results from the water-quenched samples indicated that thermal shocking did, however, affect Young's modulus; as the temperature was increased there was a slight trend towards lower values of Young's modulus. The reduction is probably due to a change in the stiffness of the composite caused by introduction of cracks. Because cracks form as a result of quenching, the change in Young's modulus may be attributed to the degree of cracking. For a fixed temperature differential, ΔT, however, the applied thermal stress will be the same and the amount of cracking would,

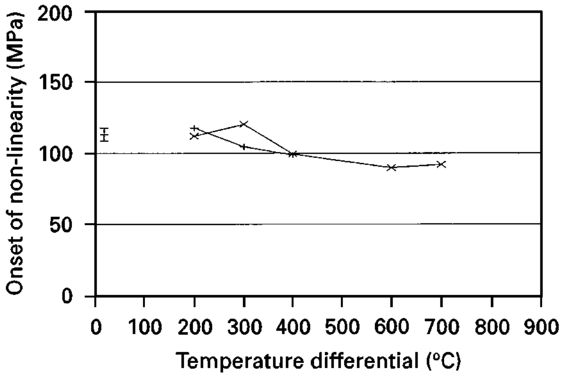

Figure 10 Onset of non-linear behaviour of thermally treated $[0/90]_{3s}$ Nicalon/CAS: (×) 1 h, (+) 6 × 1 h quenching.

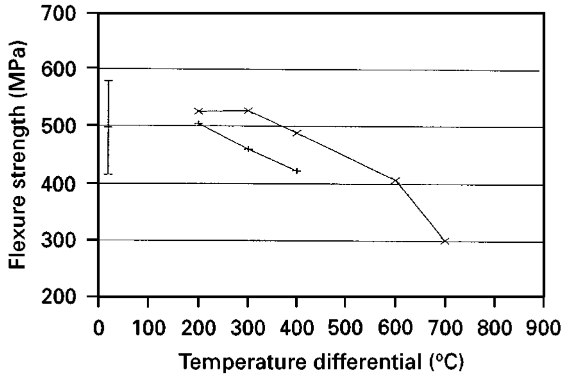

Figure 11 Flexure strength of thermally treated $[0/90]_{3s}$ Nicalon/CAS: (×) 1 h, (+) 6 × 1 h quenching.

therefore, also be expected to be similar, resulting in similar values of Young's modulus. Fig. 1 indicates that this is not the case and variations must, therefore, be as a consequence of a combination of thermal ageing and quenching.

It has been proposed previously [5, 16, 17] that interfacial sliding resistance may decrease due to oxidation of the carbon-rich interphase after ageing at 650 °C but at a temperature of 800 °C the formation of silica bridging, clamping the fibres to the matrix, may have already begun. The effect of this would be for cracks to be more easily introduced into the matrix of the composite with a weaker interface, i.e. 650 °C. The observed partial recovery in Young's modulus after thermally shocking from a temperature differential of 800 °C may be due to the silica but, after longer duration of ageing at this temperature, an increasing volume of silica may become detrimental to the composite by making it more notch-sensitive.

Crack-density measurements reported previously [5] indicated that cracks became visible on the side faces of the sample at approximately $\Delta T = 400\,^{\circ}\mathrm{C}$ and that for more severe shocks there was an increase in crack density. The results from the repeated thermal shocking (Fig. 2) suggests that the crack length and/or the crack number may increase with each shock because the reduction in Young's modulus for these samples is, if anything, greater than that for the corresponding samples subjected to a single shock (Fig. 1).

4.1.2. Onset of non-linearity

The results for the onset of non-linearity for the thermally aged and slowly cooled samples (Fig. 3) indicated that samples exposed to elevated temperature for 1 h appear to be unaffected, possibly due to the inability of oxygen to penetrate into the interphase over such a short time. Rapid progression of the oxidative reaction down the interface surrounding the exposed fibre ends has been reported [18] although it has been demonstrated that oxygen diffusion through the matrix is a much slower process [17]. Because the region of the sample subjected to the maximum tensile stress in the bend test would be oxidized via the latter type of reaction pathway, there was, as may be expected, little change to the levels of applied stress associated with initial non-linear behaviour.

Increasing the duration of thermal ageing may lead to greater penetration of oxygen into the sample with a consequent increase in the extent of modified interphase regions. The results suggested, however, that there was a reduction in performance of the material after thermally ageing for 6 h at only 500 °C. This was prior to the often quoted temperature of 600 °C for the removal of the carbon-rich interphase by the oxidative process. Results from surface analysis experiments indicated that there was a little change to the monolithic matrix material after exposure at 500 °C; hence, the reduced performance may be as a consequence of incorporating fibres into the matrix material and subsequent thermal ageing, leading to some microstructural reorganization. The cause was more likely, however, to be an oxidative reaction in which the carbon-rich interphase was gradually removed, although the reaction was too slow to be effective for the shortest duration ageing times.

This trend in the level of stress required to cause non-linear behaviour in thermally aged unidirectional Nicalon/CAS was similar to that reported by Pharoah *et al.* [17] and these two studies seem to suggest that silica may also be formed at lower temperature but is only effective in strengthening the interphase after longer periods of thermal ageing (100 h).

The onset of non-linearity for the thermally shocked samples followed a similar trend to that displayed by the slowly cooled samples, except for a very low value after thermally shocking from $\Delta T = 500\,^{\circ}\mathrm{C}$ after 24 h thermal ageing. The higher levels of applied stress sustained by the thermally shocked samples before non-linear behaviour was observed, may be as a result of cracks introduced into the material by thermal shock. Thermal shocking the samples would be expected to propagate the larger flaws inherent in the material, hence it may then require stresses greater than the matrix cracking stress to propagate these cracks further or to form new cracks from less significant flaws.

Matrix cracks in the thermally shocked samples were produced at the end of the thermal cycle, hence, there will be little opportunity for ingress of oxygen and the onset of non-linearity will tend to reflect a combination of the thermal history of the sample and the severity of the thermal shock. The apparently anomalous value after 24 h thermal ageing at 500 °C followed by quenching in water may be, at least partially, accounted for by a decrease in the amount of interphase that remains intact after the extended thermal ageing period. It is, therefore, hypothesized that this type of thermal regime, i.e. low ageing temperature but for long duration, may be the least effective in preventing matrix cracking.

Non-linear behaviour occurs at a lower level of stress in the samples receiving the same amount of thermal ageing but multiple shocks; hence, it is suggested here that the effect of each successive quench is to propagate the existing cracks, allowing ingress of oxygen further into the sample.

4.1.3. Flexure strength

The matrix continues to crack progressively during the flexure test as the load is increased above that required to produce non-linear behaviour. Hence, the flexure strength or modulus of rupture (MOR) will be controlled, primarily, by the fibre properties, although there will be an influence from the interface in determining the degree of fibre debonding and subsequent pull-out which occurs prior to peak load.

The values of 982 MPa obtained for the flexure strength of the as-received material was considerably higher than the values reported in the literature for three-point bend tests [17, 19]. However, the result will be influenced by the volume of sample tested, the span to depth ratio of the flexure sample and the rate of loading. Although the MOR value is much greater than the ultimate tensile strength (UTS), calculated from tensile test data, of 300–500 MPa [3, 14, 20] the validity of the results from the flexure tests is supported by the findings of Steif and Trojnacki [21] where it was suggested that the ratio of MOR to UTS will increase, approaching a value of 3, for composites which fail in a graceful manner, i.e. exhibit toughness.

All thermal ageing regimes appeared to have little effect on the flexure strength of the composite (Fig. 5) although a large amount of scatter in the values for the as-received material made it difficult to draw conclusions regarding any changes due to thermal ageing. However, there appears to be a possible reduction in retained strength after ageing at 650 °C for 6 or 24 h and an improved load-bearing capability after the longest ageing at 800 °C, consistent with silica formation.

Although flexure strength is, primarily, governed by fibre properties, the low values at 650 °C may be as a consequence of a reduction in interfacial shear strength (due to oxidation of the carbon-rich interphase) leading to an increase in transfer length over which an enhanced tensile stress acts on the fibres, possibly leading to fracture at a different fibre flaw than would have been sampled if the interphase had remained stronger. The improved performance at high temperature may be due to healing of flaws on the surface of the fibres by the silica coating or a greater transfer of stress to intact matrix material via silica bridging. These results are in broad agreement with those of Pharoah *et al.* [17], although their proposal that a passivating plug of silica formed at the ends of the fibres and a protective silica layer covering the other surfaces preventing any further removal of the carbon-rich interphase at higher temperatures would not be expected to lead to the observed enhanced behaviour over the as-received material. It is suggested, therefore, that silica bridges must continue to be formed in the interphase at high temperatures by diffusion of oxygen through the matrix or from the excess oxygen still available in the fibres themselves.

The variation in pull-out lengths of fibres from unidirectional composites subjected to different thermal ageing regimes is shown in Fig. 12. These results appear to confirm the mechanisms proposed above. That is, after low-temperature thermal ageing (Fig. 12a) there was a small degree of fibre pull-out before failure occurred predominantly by interlaminar shear, whilst at intermediate temperatures (Fig. 12b) fibre pull-out was increased considerably but interlaminar shear was still apparent. On increasing the ageing temperatures still further (Fig. 12c), many fibres fractured and failure appeared to have been in a more brittle manner.

The effect of thermally shocking the samples after completion of the ageing period was also seen to confirm that modifications to the interphase has occurred prior to thermal shock. This was evidenced by a reduction in flexure strength of up to 100 MPa, from the slowly cooled sample values, after ageing at 650 °C but a recovery to similar values after short-term excursions to 800 °C thermal treatment. The samples subjected to the most severe thermal treatment, however,

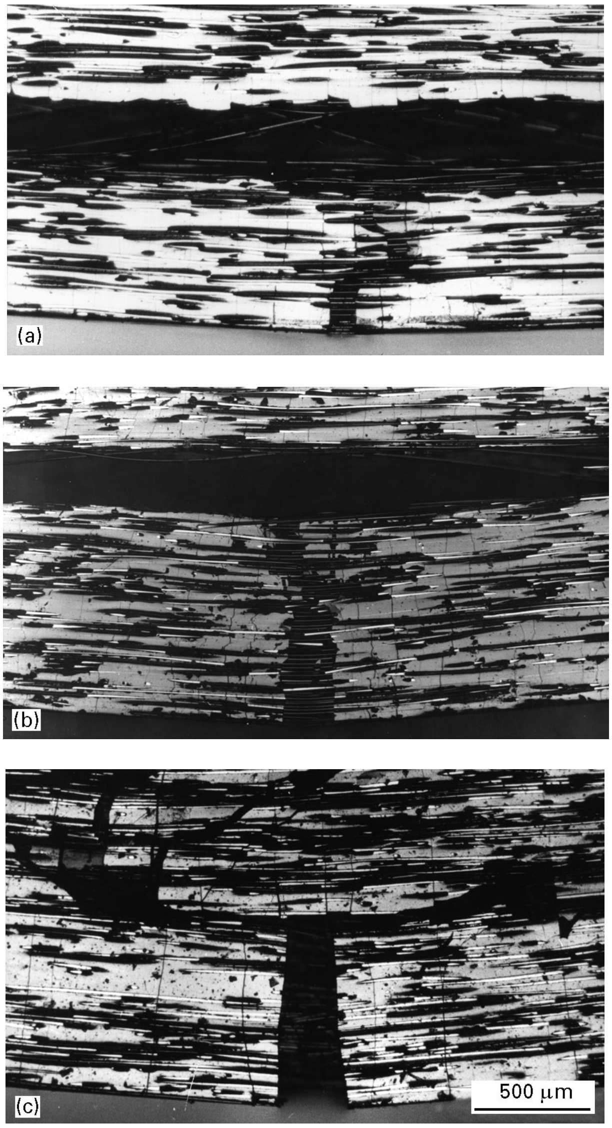

Figure 12 Reflected light photomicrographs of the effect of thermal ageing temperature on the cracking pattern in unidirectional Nicalon/CAS subjected to three-point bending: (a) 300 °C, (b) 500 °C and (c) 800 °C.

did not display this improvement. These results illustrate, again, the ease with which cracks may be introduced into the composite with a weak interphase. Although the samples quenched with a temperature differential of $\Delta T = 800\,^{\circ}C$ received a more severe thermal shock, this was compensated for in the sample quenched after 1 h by the increased crack resistance imparted to the composite by the formation of silica whilst the low strength of the 800 °C samples quenched after 6 or 24 h demonstrated that this longer duration of thermal ageing led to embrittlement and the consequent failure of fibres in the crack wake during the thermal shock process. These results are in contrast to those reported by Long *et al.* [7] where an apparent increase in flexure strength was observed after thermally shocking Nicalon-reinforced cordierite. Their experimental procedures suggested that the samples were insulated from the thermal shock process and the results were, therefore, similar to those expected for thermally aged samples.

A similar trend to that of the non-linear behaviour was observed in retained flexure strength of the multiple shocked samples. This may be accounted for by considering that the crack path generated after each thermal cycle allowed further penetration of oxygen and the subsequent sampling of longer exposed fibre lengths.

4.2. $[0/90]_{3s}$ cross-ply Nicalon-reinforced CAS

4.2.1. Young's modulus

For an equal contribution from plies of both orientations, the modulus of the $[0/90]_{3s}$ composite is calculated to be approximately 116 GPa [14]. However, this value assumes perfect bonding between fibres and matrix, whereas, for no bonding, i.e. matrix only, the transverse modulus reduces to less than 60 GPa and the composite modulus to less than 92 GPa. Since inhomogeneity within the individual plies was observed and there is unlikely to be perfect fibre/matrix bonding, the experimentally determined modulus value of 105 GPa appears in reasonable agreement with the rule-of-mixtures predictions and compares favourably with the value of 110 ± 5 GPa obtained from tensile tests on samples of a similarly configured Nicalon-reinforced CAS composite [14].

Thermally shocking samples after low temperature ($< 500\,°C$) thermal ageing appeared to have little effect on Young's modulus (see Fig. 9). Cracking damage as a result of the thermal shock was confined to the central transverse ply and was oriented parallel, not perpendicular, to the direction of subsequent applied stress. Cracks in this orientation would not be expected to affect Young's modulus appreciably and the surface plies that were subjected to the maximum tensile stresses appeared undamaged after such thermal treatments. A reduction in the modulus value following an increase in ageing temperature (i.e. 600 °C or greater) prior to thermal shock was in accord with the observed matrix cracking damage perpendicular to the fibres in the 0 °C plies.

The effect of multiple thermal shocks on the samples with a smaller temperature differential was similar to that exhibited by the unidirectional material and may also be associated with the propagation of small cracks inherent in the original material, although thermal removal of the interphase by carbon oxidation is unlikely at these lower temperatures.

4.2.2. Onset of non-linearity

The applied composite stress at the onset of non-linear behaviour in the as-received material of 113 MPa was considerably higher than values of approximately 55 MPa reported from tensile test data [22]. However, Fig. 7 indicates that the sequence of damage development in the cross-ply from bending tests is different from that observed from tension tests [22]. In particular, the mechanism of damage onset reported from tension was a crack in the central 90 °C plies and these plies are only lightly stressed in the flexure test.

The observed cracking sequence for samples subjected to three-point bending is related to the geometry of the sample because the stress is at a maximum on the tensile surface, falling to zero at the neutral axis. The calculated stress of 113 MPa at the surface of the composite assumes, however, a homogeneous beam, whereas the cross-ply consists of longitudinal and transversely oriented plies. For a homogeneous beam, the bending moment is related to the maximum stress by

$$M = \frac{4}{3}\frac{\sigma^{h}_{max}}{E}\frac{b}{d}\left(E\frac{d^3}{8}\right) \quad (3)$$

while allowing for the layered structure of the cross-ply we find

$$M = \frac{4}{3}\frac{\sigma^{c}_{max}}{E_L}\frac{b}{d}[E_L(y_6^3 - y_5^3 + y_4^3 - y_3^3 + y_2^3 - y_1^3) + E_T(y_5^3 - y_4^3 + y_3^3 - y_2^3 + y_1^3)] \quad (4)$$

where E_T is the modulus of the transverse plies and y refers to the distance of the ply interfaces from the centre of the beam. Allowing for the layered structure of the cross-ply composite thus modifies the maximum stress value on the tensile surface of the beam by a factor

$$\frac{\sigma^{c}_{max}}{\sigma^{h}_{max}} = \frac{E_L d^3}{8[E_L(y_6^3 - y_5^3 + y_4^3 - y_3^3 + y_2^3 - y_1^3) + E_T(y_5^3 - y_4^3 + y_3^3 - y_2^3 + y_1^3)]} \quad (5)$$

Typically, the true surface stress will be increased by a factor of 1.13 compared with the nominal value, i.e. from 113 MPa to 128 MPa. Although the stress distribution within the sample will be dependent upon Young's modulus of each ply orientation, the strain profile will remain linear. The stress applied to the matrix in each of the 0° plies can then be obtained via the constant strain relationship, $\sigma_m = \sigma_o E_m E_o$, whilst that in the matrix of the 90° plies will remain unaltered if the transverse modulus is assumed to be similar to the modulus of the matrix material. By adding a value of 58 MPa for the residual tensile stress in the matrix of the 0° piles [23] the total matrix stress for plies of this orientation can be determined easily. The total stress in the matrix of the 90° plies, however, is more difficult to obtain. A calculated value of approximately 23 MPa (tensile) for the residual in-ply stress, associated with the mismatch in coefficients of thermal expansion between the plies, has been reported [22, 23]. However, a contribution from the residual stress due to the mismatch in thermal expansion coefficients between fibre and matrix also needs to be considered. Using the relationship

$$\varepsilon = \Delta\alpha\Delta T \quad (6)$$

where $\Delta\alpha = \alpha_m - \alpha_f = 1.3 \times 10^{-6}\,K^{-1}$ and $\Delta T = 1200\,°C$ gives a value for $\varepsilon = 0.16\%$. However, by taking into account possible modifying effects, for example, the relative Young's moduli and volume fractions, a more realistic value for the average residual thermal strain throughout the matrix may be of the order of one half of this, i.e. 0.08%. This matrix strain then converts to a residual stress of approximately 70 MPa in the matrix and, adding this to the in-ply stress value of 23 MPa, gives a total residual stress of 93 MPa. The complete stress profile of the tensile half of a typical bend test sample at the onset of non-linear behaviour is depicted in Fig. 13.

It has been suggested [15] that a matrix stress of approximately 170 MPa is required to create cracks in either ply orientation. The values shown in Fig. 13 suggest that this level of matrix stress is attained in the 90° ply furthest from the neutral axis and this ply would, therefore, be the first to crack. Fig. 14 appears to indicate that this was not the observed cracking sequence, as numerous cracks were seen to cross the 0° plies and the ply interfacial region but were arrested after penetrating only a few fibre diameters into the transverse ply. This effect could be explained by suggesting that the interface between the matrix and fibres acts to reduce the stress concentration, blunting the advancing crack tip sufficiently to prevent further crack growth. However, the 90° plies would be expected to crack prior to the adjacent 0° plies with the crack front proceeding towards the longitudinal plies.

The tensile composite stress of approximately 55 MPa for the onset of non-linear behaviour [22], calculated from stress/strain curves generated from tensile and four-point flexure tests, was much lower than the value of 128 MPa obtained in this study. As indicated earlier, this difference is due to the geometry of the flexure test sample because only the 0° surface ply will be subjected to the maximum applied stress and the sample may behave, initially, more like the unidirectional material. The three-point flexure test also samples a smaller population of flaws and this effect would contribute to a higher stress level being attained at the onset of non-linear behaviour from flexure testing compared to that determined from tensile testing.

Thermal shock appeared to have minimal effect on the stress required to induce non-linear behaviour. This result would not be expected as it had been suggested previously that the interphase would probably undergo detrimental oxidative reactions at the elevated temperatures used in this study [24]. The appearance of samples after thermal shock treatment indicated that cracking was confined to the central plies, i.e. no surface cracks. The stress to initiate cracks, therefore, may be determined by the properties of the components of the composite, particularly the matrix, and may be similar to that required for the as-received material.

4.2.3. *Flexure strength*

The flexure strength of the as-received $[0/90]_{3s}$ cross-ply material was 500 MPa compared to a value of 980 MPa for the unidirectional composite. This difference is consistent with the factor of two difference in the proportion of longitudinal load-bearing fibres in the two lay-ups, supporting the view, e.g. [22], that fibres in the transverse direction have little effect on the strength of the composite.

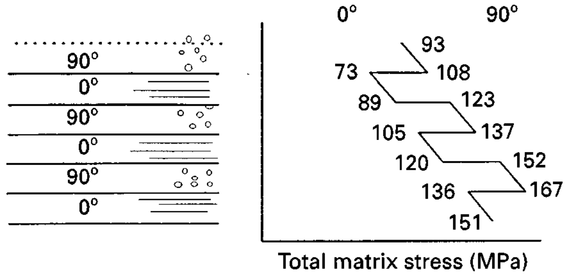

Figure 13 Schematic representation of $[0/90]_{3s}$ Nicalon/CAS in three-point bending showing stress profile in the tensile side face at onset of non-linear behaviour.

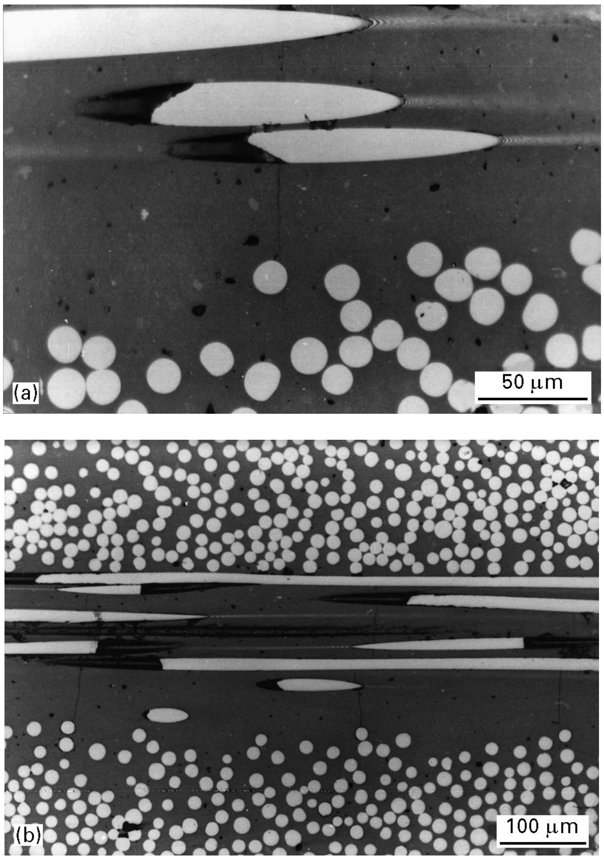

Figure 14 Reflected light photomicrographs of $[0/90]_{3s}$ Nicalon/CAS showing (a) a crack in 0° ply, and (b) cracks not penetrating the 90° plies.

5. Conclusion

The mechanical properties (i.e. Young's modulus, onset of non-linearity and flexure strength) of a unidirectional and a cross-ply $[0/90]_{3s}$ silicon carbide fibre-reinforced calcium aluminosilicate glass-ceramic composite have been determined after the composites have been subjected to various thermal regimes, ending either with slow cooling or quenching into water. For the thermally aged and slowly cooled unidirectional composite there was little change to Young's modulus over the whole temperature range (i.e. to a maximum temperature differential of 800 °C) although there was a trough in stress levels at both the onset of non-linear behaviour and flexure strength at intermediate temperatures, followed by some recovery at higher temperatures. The lower values at onset of non-linear behaviour were attributed to a reduction in resistance to matrix cracking due to oxidation of the carbon-rich interphase whilst the recovery was probably due to strengthening by formation of a silica-rich interphase. Although flexure strength is controlled primarily by fibre properties, there was probably some modification to the interphase leading to a change in stress transfer between fibres and matrix which resulted in the observed range of retained strength.

Thermally shocked samples exhibited a decrease in stiffness with increasing severity of thermal shock. This was attributed to the presence of cracks introduced by the thermal shock process following modifications to the interphase by oxidative reactions during thermal ageing. It is suggested also that the unexpected feature of increased values of applied stress required to cause non-linear behaviour in some thermally shocked samples compared to those aged for the same duration may be due to greater difficulty in propagating existing cracks or in initiating new cracks than in samples of uncracked material. This same mechanism was also suggested as a reason for a similar trend apparent in flexure strengths. The effect of multiple thermal shock cycles was to accelerate the rate of atmospheric oxygen ingress into the bulk of the samples by increasing the number and length of pathways, thus promoting interfacial oxidative reactions leading to an increase in the observed rate of deterioration in mechanical properties.

Similar results were obtained from the cross-ply composite. Young's modulus measurements on as-received material indicated a value of 105 GPa compared to the unidirectional value of 120 GPa. Thermally shocked samples showed a reduction in modulus for temperature differentials greater than 500 °C, similar to the trend exhibited by the unidirectional material. Although multiple quenching from low values of ΔT appeared to have minimal effect on the modulus of the unidirectional composite, a pronounced reduction to 86 GPa was observed at $\Delta T = 400\,^{\circ}\mathrm{C}$ which is similar to the value obtained after a single quench from 640 °C. It was suggested that this decrease in modulus at temperature differentials below that required for the unidirectional material was due to larger inherent flaws in the cross-ply composite, probably caused by difficulties encountered in processing the more complex configuration.

The applied stress at the onset of non-linear behaviour in the cross-ply material appeared to show little variation for all thermal regimes and this is attributed to the different damage patterns caused by thermal shock or mechanical loading. Flexure strength of as-received cross-ply material is approximately 50% that of the unidirectional composite mainly because the fibres in the transverse direction have little effect on the overall strength. The flexure strength values of quenched samples exhibited a similar trend to the unidirectionally reinforced material.

References

1. J. AVESTON, G. A. COOPER and A. KELLY, in "Proceedings of The National Physical Laboratory", Paper 2 (IPC Science and Technology Press, 1971) pp. 15–25.
2. D. B. MARSHALL and A. G. EVANS, *J. Am. Ceram. Soc.* **68** (1985) 225.
3. D. S. BEYERLE, S. M. SPEARING, F. W. ZOK and A. G. EVANS, *ibid.* **75** (1992) 2719.
4. A. W. PRYCE and P. A. SMITH, *Acta Metall. Mater.* **41** (1993) 1269.
5. M. J. BLISSETT, P. A. SMITH and J. A. YEOMANS, *J. Mater. Sci.* **32** (1997) 317.
6. M. J. BLISSETT, PhD thesis, University of Surrey (1995).
7. M. C. LONG, R. E. MOORE, D. E. DAY, J. G. WESTLING and R. BURNS, *Ceram. Eng. Sci. Proc.* **10** (1989) 1231.
8. Y. KAGAWA, N. KUROSAWA and T. KISHI, *J. Mater. Sci.* **28** (1993) 735.
9. Y. R. WANG and T. W. CHOU, *ibid.* **26** (1991) 2961.
10. D. LEWIS, C. BULIK and D. SHADWELL, *Ceram. Eng. Sci. Proc.* **6** (1985) 507.
11. D. C. PHILLIPS and R. W. DAVIDGE, *Br. Ceram. Trans J.* **85** (1986) 123.
12. G. D. QUINN and R. MORRELL, *J. Am. Ceram. Soc.* **74** (1991) 2037.
13. R. W. DAVIDGE, "Mechanical Behaviour of Ceramics" (Cambridge University Press, 1979).
14. A. W. PYRCE and P. A. SMITH, *J. Mater. Sci.* **27** (1992) 2695.
15. S.-W. WANG and A. PARVIZI-MAJIDI, *ibid.* **27** (1992) 5483.
16. M. H. LEWIS and V. S. R. MURTHY, *Compos. Sci. Technol.* **42** (1991) 221.
17. M. W. PHAROAH, A. M. DANIEL and M. H. LEWIS, *J. Mater. Sci. Lett.* **12** (1993) 998.
18. M. H. LEWIS, A. M. DANIEL, A. CHAMBERLAIN, M. W. PHAROAH and M. G. CAIN, *J. Microsc.* **169** (1993) 109.
19. S. M. BLEAY, V. D. SCOTT, B. HARRIS, R. G. COOKE and F. A. HABIB, *J. Mater. Sci.* **27** (1992) 2811.
20. C. M. A. DAVIES, B. HARRIS and R. G. COOKE, *Composites* **24** (1993) 141.
21. P. S. STEIF and A. TROJNACKI, *J. Am. Ceram. Soc.* **77** (1994) 221.
22. D. S. BEYERLE, S. M. SPEARING and A. G. EVANS, *ibid.* **75** (1992) 3321.
23. A. W. PRYCE and P. A. SMITH, *Acta Metall. Mater.* **42** (1994) 861.
24. R. F. COOPER and K. CHYUNG, *J. Mater. Sci.* **22** (1987) 3148.

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