JOURNAL OF MATERIALS SCIENCE 24 (1989) 199–204

Microscopic deformation in a heated unidirectional graphite–epoxy composite

W. L. MORRIS, R. V. INMAN, B. N. COX
Rockwell International Science Center, 1049 Camino Dos Rios, Thousand Oaks, California 91360, USA

Out-of-plane displacements caused by heating of a unidirectional P75S/1962-ERLX graphite–epoxy composite were measured on a surface cut normal to the fibres after thermal cycling. On heating to 44° C from room temperature, the epoxy confined within clusters of three fibres sank in a trough beneath the plane of the fibre ends by 50–120 nm. The sense of the deformation was the opposite of what one would expect from differential thermal expansion. The role of residual stresses in this deformation was studied by measuring the depth of the trough for several different thermal histories applied before the free surface was cut. When the maximum temperature achieved in the prior thermal cycles exceeded 100° C, the depth of the trough increased. However, if cycles exceeding 100° C were followed by thermal cycles of decreasing amplitude, chosen to induce interfacial stress relaxation, the depth of the trough decreased, as expected. The experiments illustrate the feasibility of deducing quantitative information about local deformation in the interior of a specimen from high spatial resolution strain measurements on cut surfaces.

1. Introduction

The best mechanical properties of non-brittle, fibrous composites are usually obtained with a good mechanical bond between the fibres and the matrix. For graphite–epoxy (GE) composites, precoating fibres has been eminently successful in achieving this condition. Nevertheless, the interfaces remain vulnerable to crack initiation and growth, particularly during thermal cycling, when interfacial stresses are generally very large. In several GE composites, the matrix flows plastically around the fibres during thermal excursions near room temperature, even when the matrix is a so-called "brittle" epoxy [1–4]. Local plastic strains approaching 10% have been found around individual fibres in 3501-5A and 934 epoxies, using high spatial resolution, stereoscopic measurements of differential displacements [1, 2]. Apart from these studies, only transparent resins containing isolated fibres [5, 6], thin films [7], or cross sections [8] have provided experimental access to the strains in the vicinity of interfaces, and even those few data have been primarily qualitative. Because of this lack of direct experimental evidence, theoretical efforts to illuminate the interfacial stresses in fibrous composites [9–11] and to calculate composite properties [12, 13] and the interfacial cracking state [14, 15] have not represented localized plasticity correctly.

Stereoscopy is unique in its ability to resolve deformation over gauge lengths comparable to or smaller than the microstructure of typical polymer composites [16–18]. The required spatial resolution of $\sim 1\,\mu m$ is well beyond the power of other, more conventional techniques such as X-ray diffraction, Moiré interferometry, or birefringence. Unfortunately, stereoscopy and related automated imaging techniques [16] measure only differential surface displacements. If stereoscopic measurements are made on a cut section, a model is needed to deduce the true internal stress–strain behaviour from differential strains that have been modified by the presence of the surface. The free surface allows out-of-plane displacements and a redistribution of the in-plane stresses. Furthermore, a singularity in certain derivatives of the surface displacements, which is not present in the interior of the material, arises on the free surface at perfectly-bonded fibre–matrix interfaces. In spite of such strong surface effects, evidence of the stress state induced by thermal cycling of GE composites before a free surface is cut may still be discernible in the surface deformation. For this to be so, residual stresses developed during the bulk deformation must by only partially relaxed when the new surface is cut; and plastic flow provoked by further surface stress relaxation during the measurement heating cycle must not obscure the effect of these residual stresses. In this paper are reported the results of a search for conditions of thermal loading of P75S/1962-ERLX that meet these prerequisites for deducing internal stresses from surface displacement measurements.

2. Experimental Procedures

Both the in-plane and out-of-plane displacements were determined in patches of the toughened 1962-ERLX epoxy bounded by three closely packed fibres approximating the geometry shown in Fig. 1a. The sites chosen for study from the many available were those with a maximum spacing $S \leqslant 0.5\,\mu m$ (Fig. 1a) between any two of the three fibres. The composite of

0022–2461/89 $03.00 + .12

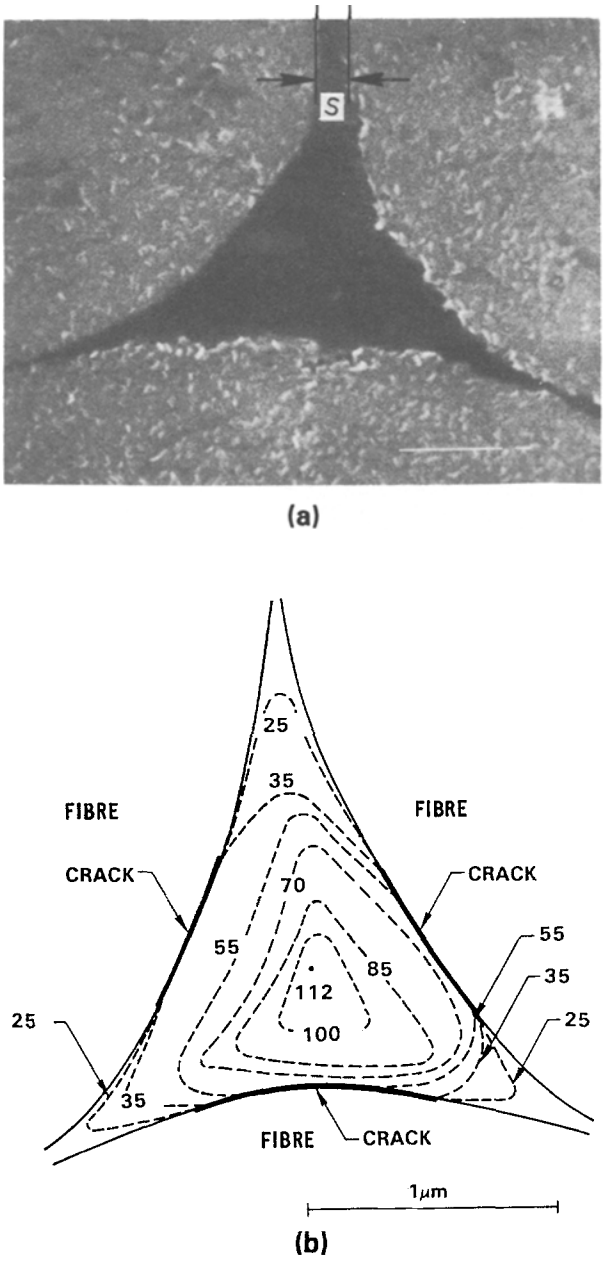

Figure 1 (a) Fibre spacing variable S, the maximum local separation between fibres, is indicated on a micrograph of a fibre cluster; (b) contour plot (in nm) of the trough formed during heating from 23 to 67° C in a specimen that had undergone three cycles of −129/+138° C before cutting for observation. In this case, S was small.

high modulus P75S fibres in 1962-ERLX was unidirectional with an average fibre volume of 60%. The unidirectional bars were sectioned normal to the fibre direction and polished after one of a selection of thermal fatigue sequences. The sectioned material was then observed during a heating of 44° C from room temperature.

Displacements generated by the heating from 23 to 67° C were determined by a stereoscopic comparison of micrographs recorded at the two temperatures. The same initial and final temperatures were used for all measurements to insure that any correlation of the displacements found with the earlier thermal sequence was caused by changes inside the specimen before it was sectioned.

The micrographs were obtained by using a heating stage in a scanning electron microscope. Two views of a surface were recorded at each temperature to allow both the in-plane and out-of-plane components to be determined. The local displacements from heating were found from these by a stereoscopic technique first described by Williams *et al.* [18]. A normal (90°) viewing angle was used to determine the in-plane displacements and a 50° viewing angle to find a mixture of in-plane and out-of-plane components from which the out-of-plane values were calculated by simple geometry (Fig. 1b). Only out-of-plane displacements are reported in this paper because they were an order of magnitude larger than the in-plane displacements. The displacement measurement accuracy set by the quality of the 30 000X SEM images was approximately ± 2 nm. A second accuracy limit that superceded this was caused by instability in the magnification of the SEM. Once the machine was allowed to stabilize, this error was $\sim \pm 5 \times 10^{-3} l_0$ for our instrument, where l_0 is the gauge length over which differential displacements were compared. The net error from both sources in out-of-plane displacement values measured relative to the fibre ends is roughly ± 7.5 nm at the centre of a three-fibre cluster.

Thermal cycling was accomplished by encapsulating 1 cm long bars of P75S/1962-ERLX in an argon environment in a quartz tube. The tube was then translated by a pneumatic actuator between hot and cold reservoirs with a period of 2–5 min/cycle. A typical experiment (Fig. 2a) involved three cycles between $T_{max} \geqslant 23°$ C and $T_{min} \leqslant 23°$ C, terminating at room temperature (23° C) during the warming phase of the cycle. Afterwards each bar was sectioned to extract an interior sample 2 mm thick. One surface of this was polished so that the local deformation could be followed during the subsequent heating to 67° C.

3. Results

The differential thermal expansion between the epoxy and the graphite fibres is very large, and cracking of portions of each fibre–matrix interface occurs on cooling from the processing temperature. This cracking is least around fibres in densely packed clusters, and such sites were chosen for further examination for this reason. Nevertheless, even in these densely packed clusters, small cracks remained at the sites indicated in Fig. 1b. These are the locations in the cluster where the distance to the nearest neighbouring fibre measured along a radius is largest.

As a sample was heated, the fibres at the surface expanded in the radial direction and the epoxy sank into a trough. The depth of the trough was a maximum at the centre of the fibre triangle.

Clearly, the free surface modifies the observed deformation, but is the plasticity present caused entirely by the measurement heating in the presence of the free surface? Probably not, because the depth of the trough changed with the maximum temperature of the thermal cycle applied before each sample was cut. Fig. 3 illustrates this effect. Each datum is the average of two to four observations of trough depths for fibre clusters for which the maximum spacing (S) between adjacent fibres (defined in Fig. 1a) was 0.4 μm or less. The error bars indicate the variance of the peak

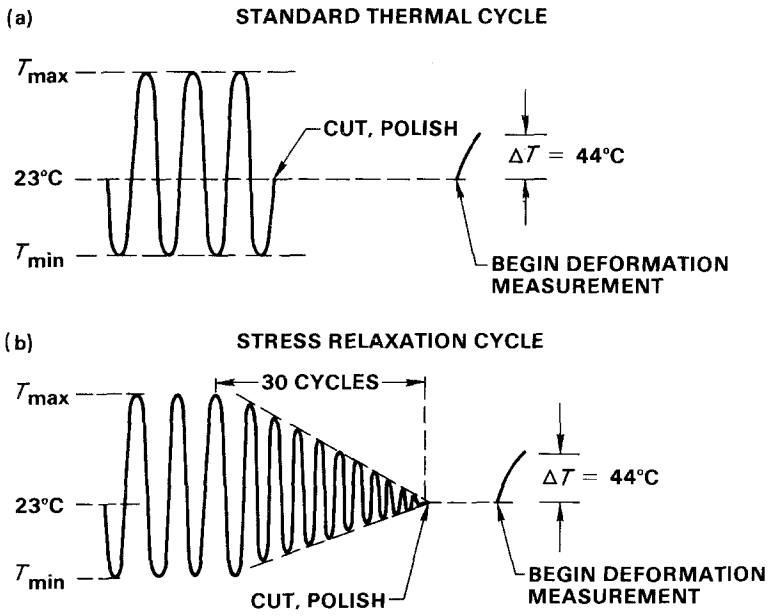

Figure 2 Thermal cycles applied prior to sectioning composite bar. (a) Standard constant amplitude cycle used to generate Fig. 3; and (b) load shedding cycle.

displacements for different clusters, rather than the measurement error, which is much smaller. No effect of T_{min} on the out-of-plane displacement was detected. (T_{min} in these studies was always 23° C or smaller.) However, for T_{max} above 100° C, the magnitude of the out-of-plane displacement of the epoxy (i.e., the trough depth) increased with T_{max}. Since the maximum temperatures refer to cycling *before* each bar was sectioned, the displacements reflect memory of changes in the bulk material.

To determine if the memory of the prior cycling was embodied in residual stresses, a thermal load sequence of decaying amplitude (Fig. 2b) was applied in an attempt to partially relax any residual stresses present. A bar was subjected to three cycles with a T_{max}/T_{min} of $+138/-128$° C to induce the same deformation as before, and then the relaxation sequence (Fig. 2b) was applied prior to sectioning. The normal displacements measured after sectioning were now indistinguishable from those generated by a sequence having T_{max} = 23° C. The memory of the prior excursions to T_{max} = 138°C was erased, and so apparently stemmed from residual stresses near the internal fibre–matrix interfaces (see the next section).

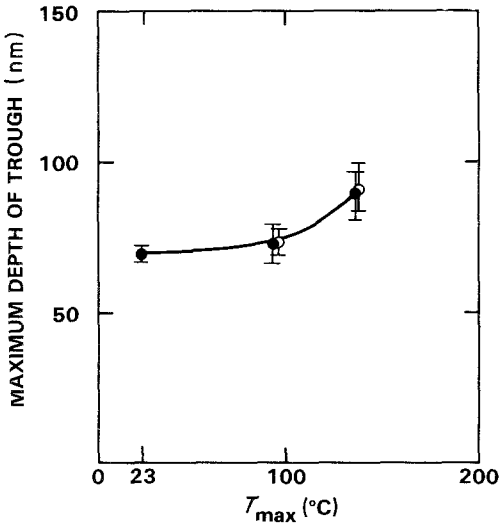

Figure 3 The depth of the trough in the epoxy relative to the fibre ends for a 44° C measurement heating interval, as a function of the maximum temperature achieved in prior thermal cycling of constant amplitude. (● T_{min} = −23° C, ○ T_{min} = −129° C).

To identify the fibre spacing for which the memory effect is most obvious, the depths of the troughs were also analysed relative to the fibre separation variable S. Two sets of data, namely cyclic loading with a small T_{max} and cyclic loading to 138° C followed by the stress relaxation thermal cycles, produced identical changes in the trough depths as a function of S (Fig. 4). Specimens that experienced a T_{max} of 138° C and suffered no stress relaxing cycles showed the greatest difference from these data at small S.

The surface deformations observed when the specimen was returned to room temperature after the first measurement heating and then repeatedly heated and cooled between room temperature and 67° C were as follows. On the first return to room temperature, the depth of the trough decreased slightly, as did the mode III crack opening displacements of the interfacial cracks such as those shown in Fig. 1. During further cycles, the succeeding differential surface displacements measured during heating were generally found at first to have the same sign as during the first measurement cycle, but with rapidly diminishing amplitude. After several cycles, the differential displacements were barely above the experimental noise.

At this stage, not all of these observations are understood. It is clear that the differential displacements depend in detail on the boundary conditions imposed by the state of bonding at the fibre–matrix interface and the presence of the free surface. However, a feasible explanation of the initial, deep trough is presented in the next section. Note especially that the formation of a trough on the first measurement heating has now been observed in various other geometries, including epoxy enclosed by a pentagonal ring of fibres and a model composite consisting of a 3 μm layer of epoxy sandwiched between two aluminium half-spaces.

One further important test was to assess the effect of moisture. It could be possible that the observed trough could be caused partly by the loss of water absorbed

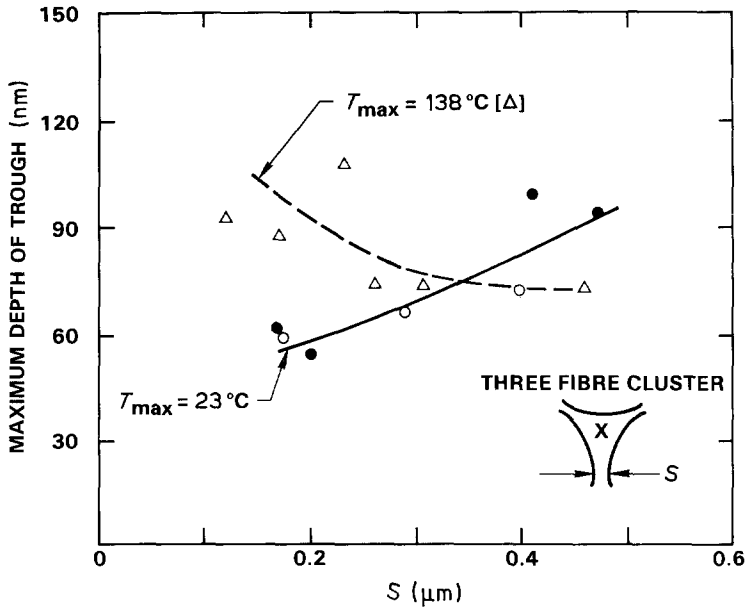

Figure 4 Dependence of the depth of the trough in the epoxy relative to the fibre ends on the fibre separation variable, S. (● three cycles to 23° C, ○ three cycles to 138° C, then decrease amplitude as in Fig. 2b)

during surface preparation. To test this conjecture, a specimen that had undergone six thermal cycles following cutting was placed in boiling water for ten minutes. No change in the normal surface displacement was caused by this treatment. Since any mass gain from water absorption had no direct effect on the displacements, it is reasonable to infer that water loss did not cause the trough observed in other measurements.

4. A tentative model of the observed trough

The formation of a trough in the resin triangle during the initial measurement heating is at first thought rather surprising. The resin has a large, positive coefficient of thermal expansion (CTE) ($> 20 \times 10^{-6}\,°C^{-1}$), whereas the graphite fibres have a slightly negative CTE in the longitudinal direction. In the absence of residual stresses, the epoxy would therefore bulge out beyond the plane of the fibre ends during heating. This would be the case whether the fibre–matrix interfaces were bonded or debonded.

However, when residual stresses are taken into account, the situation can change dramatically. After cooling down from the curing process, the mismatch in CTEs between the fibres and the resin causes the latter to bear high tensile stresses in the longitudinal direction. During thermal cycling of uniform amplitude (Fig. 2a), this longitudinal component of the residual stress may be modified in magnitude, but probably remains tensile at room temperature. Upon sectioning the specimen to prepare a surface for observation, some relaxation of the residual stresses occurs near the new surface. (No direct measurement of displacements caused by this relaxation can be made, since stereoscopy measures differential displacements only and no reference micrograph can be recorded.) Nevertheless, the residual stresses throughout the bulk and quite near the surface remain large, presumably similar in magnitude to the yield stress at room temperature, since plastic deformation is clearly observed during fairly small heatings.

When the measurement heating occurs, two competing effects are to be expected. One is thermal expansion, which, as already noted, would tend to cause the epoxy to bulge out above the cut surface. The other is flow under the driving force of the remaining residual stresses attributable to the fact that the yield stress of the resin falls with increasing temperature.

The inverse proportionality of the yield stress and temperature for epoxy resins is well documented for temperatures near the glass transition temperature, T_g [19]. As T_g is approached from below, the yield stress falls to zero. At lower temperatures, the temperature dependence is impossible to measure in tension in neat resin specimens, because they suffer brittle failure before yielding occurs. However, resin in small volumes can now be seen to show considerable plasticity in tension (e.g. Fig. 1b). Brittle failure does not occur even near room temperature during the formation of partially irreversible strains of $\sim 10\%$, perhaps because sufficiently small volumes of the resin are defect free. The sense of the deformation seen in Fig. 1b, i.e., the formation of a trough rather than a bulge, suggests strongly that the yield stress does indeed fall with increasing temperature near room temperature. As the yield stress falls, the tensile longitudinal residual stress begins to draw the resin down into the bulk. This phenomenon apparently overshadows the effects of differential thermal expansion.

It is instructive to compare the depth of the observed trough with elastostatic calculations of the bulge that would occur because of differential thermal expansion in an inclusion of geometry and properties roughly approximating those of the constrained triangle of epoxy. In the case of interfaces remaining perfectly bonded, rough estimates of the expected displacements for such a composite can be obtained from calculations for perfectly-bonded, semi-ellipsoidal surface inclusions [20]. These calculations show that, for a 44° C heating interval in such a purely elastic system possessing the known differential thermal expansions between the fibres and epoxy, the bulge height would be ~ 1.5 nm. This is about two orders of magnitude less than the observed trough depth, a

difference that highlights the magnitude of the plastic deformation.

5. Discussion

One purpose for obtaining out-of-plane displacement values for P75S/1962-ERLX was simply to determine if high resolution, stereoscopic analysis of SEM micrographs to find normal displacements is practicable. It was hoped to improve sensitivity by comparing micrographs of a tilted specimen taken at the same viewing angle, but at two different temperatures, instead of comparing micrographs taken at two viewing angles, as is usually done. This eliminates the visualization of any specimen surface roughness present prior to heating. One major concern was that instability in the dynamic focus of the microscope might obscure the tiny thermal displacements being sought. This was not the case. The procedure worked well and an analysis of pairs of micrographs recorded at two viewing angles allowed both the in-plane and out-of-plane components to be established.

The discovery of memory of prior thermal loading history in the out-of-plane deformation was made before all means of increasing the residual signal were recognized. In the future, a more symmetric and repeatable geometry to eliminate interfacial cracking and local geometric variations, and the use of a full temperature reversal for the strain measurements may make the memory of prior internal deformation more conspicuous.

Some questions about the source of the memory still remain. It is precluded by the relaxation measurements that excursions to $T_{max} > 65°C$ had either increased interfacial cracking density or somehow changed the room temperature flow stress of the epoxy. Whatever happened near the interfaces is reversible by a sequence of cycles of decaying temperature amplitude. It was also observed that increasing the local fibre spacing S decreases the memory effect (Fig. 4). One might speculate that this relationship is derived from an association between the local cracking state and the local stress range. The interface cracks are larger after cooling from the processing temperature in clusters where the spacing S is larger. If sliding at the fibre–matrix interfaces is the major factor in the memory, the displacements from sliding should have increased with S, because the crack sizes do so. However, if residual strains from plastic flow in the epoxy caused the memory, relaxing the local residual stresses with increased crack density might decrease the plastic strains and the memory effect at large S and T_{max}, as is observed.

From the simple elastic calculations of the preceding section, it can be concluded that much of the strain in the 1962-ERLX epoxy within a few tenths of microns of the fibre–matrix interfaces is plastic, even near room temperature. Similar results have been found for the epoxy 934, which is much less ductile than 1962-ERLX, which implies that such local plasticity is permitted by the smallness and constraint of the volume to which it is confined. The interface behaviour may also be affected by a thin interface coating of epoxy applied during manufacture, but no boundary which would flag the presence of this layer has been apparent in the deformation. That the interfaces can have properties substantially different from those of the bulk already has proponents in investigators who have observed plasticity in the propagation of cracks in nominally brittle resins at room temperature [21–23]. Within a few tenths of microns of the fibres, the strains in the epoxy approach 10% and the deformation is clearly plastic. It seems obvious that some amount of interfacial sliding must also accompany such large plastic flow.

Knowledge of the true local stress–strain properties of such resins is important for analysing the reliability of the fibre–matrix interfaces in extended mechanical or thermal loading. The problem to be solved to obtain these properties is not simple, but it is at least conceptually divisible into two steps, one of which has already been taken for alloys [24, 25]. Surface strains measured in individual surface grains of an aluminium alloy [24, 25] have been used to calculate each grain's mechanical properties by means of an extension [19, 24, 25] of Eshelby's [26] analysis of the deformation of an inclusion in a matrix. The procedure is to expose a sample containing a 300 μm grain to an appropriate sequence of loads. These produce a sequence of measurable strains from which the local stresses, state of constraint, and hence local flow stresses and a strain hardening coefficient can be deduced. For the composite, a model would be required of the temperature dependent elastic–plastic flow in the three-fibre cluster geometry within the bulk. Bulk thermal cycling sequences would then produce predictable residual stresses from which the local properties could be found if these local stresses were determined as a function of load sequence. The second theoretical challenge would then be to estimate from measured surface displacements of sectioned material, the internal residual stress state before the free surface was cut. This theory must consider both the consequences of the stress relaxation allowed by the free surface and any alteration of the plastic flow due to the changed condition of constraint.

6. Summary

Deformation near individual fibre–matrix interfaces of a graphite–epoxy composite is apparently microplastic at temperatures well below the bulk brittle–ductile transition temperature. The conditions under which internal residual stresses induced by interfacial flow during thermal cycling would be apparent from studies of the deformation of a surface cut subsequently normal to the fibres have been investigated. A standardized measurement of the deformation state was obtained by determining the out-of-plane displacement of epoxy included between fibre triplets for a 44° C temperature increment. Memory of the prior thermal load history was sought and found in increased trough depths in the epoxy when the cyclic temperature to which the bulk specimen had been exposed exceeded $\approx 100°C$. This memory was found to be erasable if there followed a bulk thermal loading sequence of decreasing temperature range converging to a room temperature mean. The most plausible

explanation of this result is that the memory of the prior thermal cycling is contained in residual stresses near the fibre–matrix interfaces caused primarily by localized plastic flow of the epoxy; and that relaxation of the residual stresses is enabled by the falling of the yield stress in the epoxy resin as the temperature rises during the displacement measurement. That internal residuals leave their mark on the deformation of a newly exposed surface in a GE composite gives hope that cleaner experiments and analysis may eventually allow the mechanical properties of the epoxy near the fibre interfaces to be determined. In particular, the measured depth of the trough formed by various temperature excursions following appropriately designed prior thermal cycling should allow inference of both initial local residual stresses and the temperature dependence of the yield stress.

Acknowledgements

This research was supported mainly by Rockwell International IR & D funds. Some of the final conclusions were arrived at and revisions to the paper made during the course of work under NASA Contract NAS1-18231. The support and interest of H. Rockoff and L. Crockett of Rockwell's Space Station Systems Division and D. Bowles of NASA Langley Research Center are much appreciated.

References

1. W. L. MORRIS and B. N. COX, in Proceedings of the 6th International Conference on Composite Materials, London, July 1987, edited by F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson and J. Morton (Elsevier Applied Science, London, 1987) p. 4.344.
2. W. L. MORRIS, R. V. INMAN and M. R. JAMES, *J. Eng. Mat. Tech.* in press.
3. N. SATO, T. KURAUCHI and O. KAMIGAITO, *J. Mater. Sci.* **21** (1986) 1005.
4. R. P. KAMBOUR, M. A. VALLANCE, E. A. FARRAYE and L. A. GRIMALDI, *ibid.* **21** (1986) 2435.
5. W. D. BASCOM, R. M. JENSEN and L. W. CORDNER, in Proceedings 6th International Conference on Composite Materials, London, July 1987, edited by F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson and J. Morton (Elsevier Applied Science, London, 1987) p. 5.424.
6. A. FAHMY, private communication.
7. W. W. ADAMS, D. YANG and E. L. THOMAS, *J. Mater. Sci.* **21** (1986) 2239.
8. N. SATO, T. KURAUCHI, S. SATO, O. KAMIGAITO, in Fracture Mechanics: Sixteenth Symposium, ASTM STP 868, edited by M. F. Kanninen and A. T. Hopper (ASTM, Philadelphia, 1985) p. 493.
9. D. F. ADAMS, in Advances in Composite Materials, Proceedings 3rd International Conference on Composite Materials, Paris, August 1980, edited by A. Bunsell, C. Bathias, A. Martrenchar and G. Verchery (Pergamon, Paris, 1980) p. 81.
10. Y. M. HADDAD, *J. Mater. Sci.* **21** (1986) 3767.
11. N. SATO, T. KURAUCHI, S. SATO, O. KAMIGAITO, *ibid.* **19** (1984) 1145.
12. C. C. CHAMIS, in Reinforced Plastics/Composites '84-39th Annual Conference, Houston, January 1984 (Society of the Plastics Industry, Inc., New York, 1980) p. 16.
13. D. F. ADAMS, D. E. BOWLES and C. T. HERAKORICH, *J. Reinforced Plas. Comp.* in press.
14. P. A. GRADIN and J. BACKLUND, in Advances in Composite Materials, Proceedings 3rd International Conference on Composite Materials, Paris, August 1980, edited by A. Bunsell, C. Bathias, A. Martrenchar and G. Verchery (Pergamon, Paris, 1980) p. 162.
15. V. D. KRSTIC, M. KOMAC and M. D. VLAJIC, *J. Mater. Sci.* **19** (1984) 4119.
16. B. N. COX, W. L. MORRIS and M. R. JAMES, in Proceedings of Conference on Nondestructive Testing and Evaluation of Advanced Materials and Composites, Colorado Springs, August 1986 (NTIAC, US Department of Defense, 1986) p. 25.
17. W. L. MORRIS, R. V. INMAN and M. R. JAMES, *J. Mater. Sci.* **17** (1982) 1414.
18. D. J. WILLIAMS, D. L. DAVIDSON and J. LANKFORD, *Exp. Mech.* **20** (1980) 134.
19. R. J. MORGAN, J. E. O'NEAL and D. B. MILLER, *J. Mater. Sci.* **14** (1979) 109.
20. B. N. COX, *J. Appl. Mech.* in press.
21. R. J. MORGAN, E. T. MONES and W. J. STEELE, *Polymer* **23** (1982) 295.
22. L. LORENZO and H. T. HAHN, *Polym. Eng. Sci.* **26**(1986) 274.
23. S. YAMINI and R. J. YOUNG, *J. Mater. Sci.* **15** (1980) 1823.
24. W. L. MORRIS, B. N. COX and M. R. JAMES, *Acta. Metall.* **5** (1987) 1055.
25. B. N. COX, W. L. MORRIS and M. R. JAMES, *ibid.* **5** (1987) 1289.
26. J. D. ESHELBY, *Proc. R. Soc. A* **241** (1957) 376.

Received 3 November 1987
and accepted 25 February 1988