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# The durability of controlled matrix shrinkage composites

## Part 3 *Measurement of damage during fatigue*

P. W. K. LAM*, M. R. PIGGOTT
*Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A4*

During fatigue of aligned fibre pultrusions, the flexural modulus decreases continuously when the applied stresses are tensile and directed along the fibres ($R = 0.1$). In addition, the Poisson's ratio increases continuously, and so does the energy absorbed during the fatigue cycle. Holes in the specimens continuously increase in size in a direction at right angles to the applied stress, but change little in the stressing direction. These effects are enhanced by including compressive stresses in the cycle ($R = -0.3$) and are reduced by reducing the polymer cure shrinkage pressure. There are notable similarities between fatigue failure and compressive failure in aligned fibre composites, and evidence that matrix stresses are produced at right angles to the fibres, which are probably large enough to cause matrix fatigue failure. These observations lead to the conclusion that the fatigue failure may well originate from misaligned fibres, which generate off-axis stresses. These cause interface failure and polymer fragmentation, which can then lead to fibre failure (and thus composite failure) even when the applied stresses are always tensile.

## 1. Introduction

In the earlier papers of this series it was shown that carbon-reinforced epoxies, made with the aid of special additives which reduced the cure shrinkage stress of the polymer, had improved toughness without loss of shear strength [1]. In addition, the fatigue properties of the composites were improved [2].

The shrinkage was controlled by adding expanding monomers, dinorbornene spiro orthocarbonate (DNSOC) or tetramethyl spiro orthocarbonate (TMSOC) to the epoxy, and making copolymers. Reduction of shrinkage using a plasticizer, dimethyl formamide (DMF) instead, was not effective. With moderate additions of DNSOC or TMSOC the resin properties were not significantly affected.

The effect of the shrinkage stress on the fatigue properties was to change the slope of the *S–N* curve. Reducing the shrinkage stress reduced the slope under all conditions tested, i.e. tension, $R = 0.1$, tension–compression, $R = -0.3$ and compression, $R = -\infty$, when expanding monomers were used. Again, the plasticizer did not give any beneficial effect.

Control of polymer shrinkage without any apparent change in any other parameter has not hitherto been possible. It thus provides a new means of investigating the fatigue failure process in carbon-fibre composites. So far, fatigue failure has mainly been investigated by observation of damage processes that occur in laminates, e.g. cross-ply [3] or unidirectional, [4], or more complex structures [5]. Some progress has been made in describing the events that accompany failure, but little progress has been made in relating basic materials properties (e.g. fibre Young's modulus) to fatigue properties. Although it has been suggested that there could be an endurance limit, given by the endurance limit for the polymer, in terms of strain [3], there does not appear to be any data on these endurance limits, nor any attempt to explain the different slopes of the *S–N* curves of different carbon–epoxies or other reinforced polymers.

In the hope of further clarifying the causes of fatigue failure, in this paper we will examine a number of different indicators of damage accumulation during fatigue, and how they are influenced by shrinkage pressure and other variables.

## 2. Experimental method

The experiments were carried out on pultrusions made with a fibre volume fraction of about 0.5, as described previously [1] using carbon fibres (Hercules AS1). The polymers used contained different amounts of the two expanding monomers mentioned in Section 1, i.e. DNSOC and TMSOC. Some polymer matrices contained, instead, the non-reactive plasticizer DMF. Also, for some experiments the fibres were coated with silicone fluid (Dow Corning DC 20) before immersion in the epoxy resin. Further details of the materials and techniques used may be found in Part 1 of this series [1].

Prior to the fatigue tests, the samples were end-tabbed and screened by preloading to 80% of their mean UTS. The survivors were fatigued in an MTS

**Present address*: Nova Huskey Research Corporation, 2928 16th Street, N.E., Calgary, Alberta T2E 7K7, Canada.

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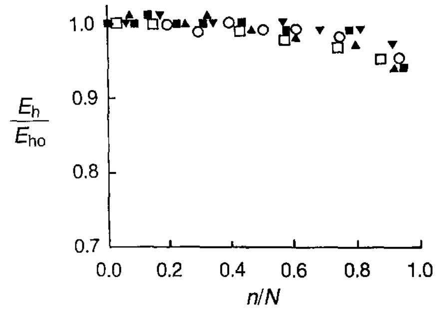


*Figure 1* Change in Young's modulus during fatigue, $R = 0.1$. Results plotted include composites made with and without spiro and DMF, and composites made with silicone-coated fibres. (○) E815, no additive, 920 MPa; (■) E815, 10% TMSOC, 920 MPa; (▼) D332, 15% DNSOC, 800 MPa; (▲) E828, 20% DMF, 800 MPa; (□) E815, silicone, 800 MPa.

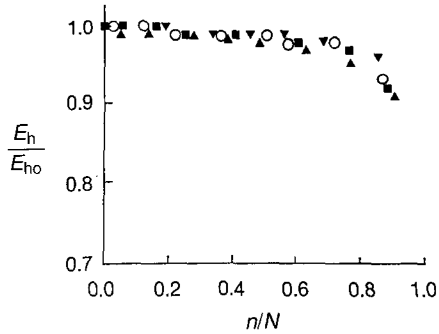


*Figure 2* Change in Young's modulus during fatigue, $R = -0.3$. Results plotted include composites made with and without spiro and DMF. (○) E815, no additive, 670 MPa; (■) E815, 10% TMSOC, 700 MPa; (▼) D332, 15% DNSOC, 750 MPa, (▲) E828, 20% DMF, 600 MPa.

machine at 10 Hz at constant amplitude at stress ratios $R$ of 0.1, $-0.3$ and $-\infty$. For higher stresses (lives less than 1000 cycles), 2 Hz was used. Four stress levels were used, with five replicate tests at each stress level, and the results analysed using a statistical method [5]. In the work described here, specimens were removed from the machine during the fatigue tests, and various measurements made on them, as described below. In addition, some specimens were monitored while being fatigued.

The axial Young's modulus, $E_1$, was measured using an extensometer in a quasi-static test. $E_1$ was also determined from the orientation of the hysteresis loop in the fatigue test. Both methods gave the same result within experimental error, so for most of the results presented here the hysteresis loop method was used. The hysteresis loop was also used to determine the energy, $H$, absorbed by the specimen during fatigue. For this, the loop area was measured using a planimeter. The Poisson's ratios, $\nu_{12}$, of some specimens were measured by fixing 120 Ω foil strain gauges on to the specimens using epoxy glue. They were oriented so that they measured the transverse strains. The resistance of the strain gauge was monitored using a Vishay-Ellis 20 digital strain indicator. The longitudinal strain was estimated from the current Young's modulus and the load, and Poisson's ratio determined by the rato of the two strains.

The residual strengths, $\sigma_{1u}$, of some of the specimens were measured in a quasi-static tensile test at various fractions of the fatigue life. This was done in the MTS machine at a constant loading rate of 0.1 kN sec$^{-1}$. Similarly, shear strengths, $\tau_{12u}$, were measured using the short beam shear method (ASTM D2344) at a constant cross-head speed of 1.0 mm min$^{-1}$ in an Instron machine in three-point bending. The span to thickness ratio used was 5 to 1. Flexural modulus, $E_{fl}$, was monitored during fatigue, also using three-point bending in the Instron machine at 1.0 mm min$^{-1}$, but with a span to thickness ratio of 16 to 1. At least three replicates were used for all the above tests.

Some specimens, prior to the fatigue test, had holes $4.55 \pm 0.05$ mm carefully drilled through their centres. A high-speed drill was used, and the composite was protected by 3 mm thick aluminium sheets on both sides during the drilling. The hole size was monitored during the fatigue test, in both the axial and transverse directions.

Finally some specimens were made by the hand lay-up process, and some of these had Teflon patches moulded inside, at the centre. These specimens were otherwise as similar as possible to the pultrusions.

## 3. Experimental results

The Young's moduli of the composites were very little affected by the stresses in tension–tension fatigue,

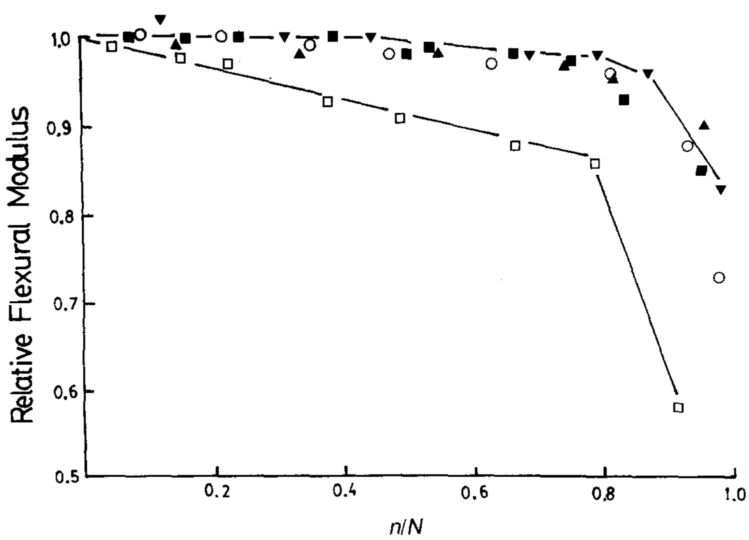


*Figure 3* Change in flexural modulus during fatigue, $R = 0.1$. Results plotted include composites made with and without spiro and DMF, and composites made with silicone-coated fibres. (○) E815, no additive, 920 MPa; (■) E815, 10% TMSOC, 920 MPa; (▼) D332, 15% DNSOC, 800 MPa; (▲) E828, 20% DMF, 800 MPa; (□) 815, silicone, 730 MPa.

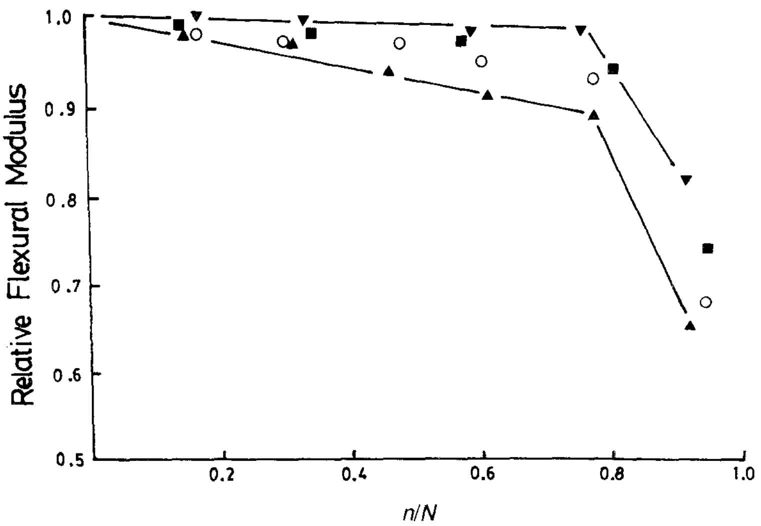


*Figure 4* Change in flexural modulus during fatigue for composites made with a Teflon patch at the centre, $R = 0.1$. (○) E815, no additive, 920 MPa; (■) E815, 10% TMSOC, 920 MPa; (▼) D332, 15% DNSOC, 800 MPa; (▲) E828, 20% DMF, 800 MPa.

$R = 0.1$, up to half the fatigue life ($n/N = 0.5$, Fig. 1, where $n$ is the number of cycles and $N$ is the average number of cycles to failure. E815 and E828 are Shell EPON 815 and 828, D332 is Dow DER 332; all are epoxy resins. 800 and 920 MPa refer to the maximum stresses in the fatigue experiment). Thereafter some decline could be observed, most notably with the composites made with epoxy containing DMF, and with silicone-coated fibres. Near the end of their lives the moduli started to decrease sharply, and when last measured the specimens had lost 2.5 to 5.8% of their stiffness. The smallest loss was for the matrix with the lowest shrinkage stress (epoxy containing 15% DNSOC). Losses in $E_1$ were greater when there were compression stresses, $R = -0.3$, Fig. 2. Again the lowest loss was for the resin with the smallest shrinkage, and the highest loss was with the DMF. (Composites with silicone-coated fibres were not included in this test.)

The flexural moduli decreased somewhat more than the Young's moduli, Fig. 3. Again the smallest loss rate was observed with the resin having the lowest cure shrinkage, and the greatest with the composites made with silicone-coated fibres. The sharp decline in modulus near the end of the fatigue life was more marked in the flexural test than in the tensile test. Having a Teflon patch inside the specimen hardly affected the rate of flexural modulus loss, Fig. 4.

The Poisson's ratios, $\nu_{12}$, increased during fatigue, Fig. 5. The rate of change in $\nu_{12}$ for the different resins correlated well with the modulus losses. This experiment had to be terminated earlier than the modulus experiments because the epoxy adhesive failed at a relatively early stage, and the strain gauge separated from the specimen.

Hysteresis loop energies increased during fatigue, Fig. 6. The rate of increase was somewhat greater when compression was involved ($R = -0.3$); compare Figs 6 and 7. The centre holes increased in size in the $y$-direction, i.e. transverse to the stress, Fig. 8, top. Cracks appeared, and gradually got wider as the fatigue test proceeded. The hole hardly changed at all in size in the direction of the stress (the $x$ direction), Fig. 8 bottom. The differences between the different matrices were not very noticeable in the $x$-direction, in marked contrast with the $y$-direction. These results were for $R = 0.1$; similar results were obtained for $R = -0.3$, except that the effects were larger, Fig. 9.

Residual strengths were only measured at one point on the $S$–$N$ curve. The values of the maximum stress (or minimum stress for compression) and number of cycles chosen for the sampling were such that at least half the fatigue life was expended. The effects on tensile strength, Fig. 10, and shear strength, Fig. 11, were relatively small, especially with the DNSOC copolymer. In these figures residual strengths relative to the initial strength are plotted, with initial strengths inset.

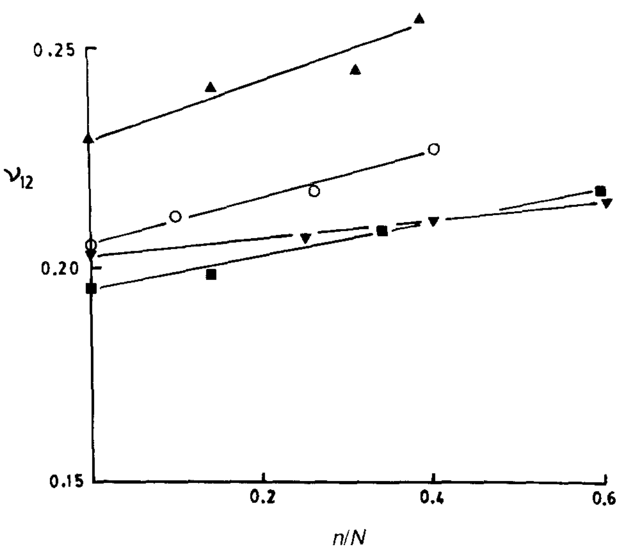


*Figure 5* Change in Poisson's ratio during fatigue, $R = 0.1$. For key, see Fig. 4.

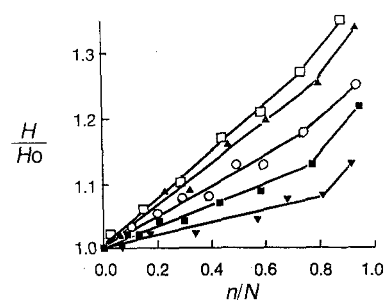


*Figure 6* Change in hysteresis loop energy during fatigue, $R = 0.1$. For key, see Fig. 1.

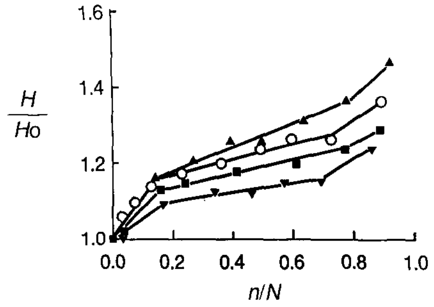


*Figure 7* Change in hysteresis loop energy during fatigue, $R = -0.3$. For key, see Fig. 2.

## 4. Discussion

It is evident from the hysteresis loop energy (Figs 6 and 7) and hole size growth (Figs 8 and 9) that, even with aligned fibre composites, fatigue is a process in which damage accumulates continuously. The degradation is greater for $R = -0.3$ than $R = 0.1$. This damage is not very apparent, however, when Young's modulus, or residual tensile strength is monitored (Figs 1, 2, and 10), though it is revealed quite well by the flexural modulus (Figs 3 and 4).

The slope of the $S$–$N$ curve, $\beta$, is a good indicator of damage rate; it correlates well with the rate of increase in hysteresis loop energy, Fig. 12, and rate of increase in hole size, Fig. 13. (Full details of the experiments in which $\beta$ is measured are given in Part 2 of this series [2].)

The damage is evidently mainly confined to the matrix and the interface, because little change is seen in tensile properties. The interface plays a major role, because reducing the adhesion between fibres and matrix caused an anomalously large rate of loss of flexural modulus: see Figs 3 and 14; fibres silicone coated.

Perhaps the most important clue to the damage mechanism comes from the Poisson's ratio, Figs 5 and 15. This increases as fatigue proceeds, indicating some loss of continuity of stress normal to the applied stress. Also the holes grow normal to the stress. These two observations strongly indicate a gradual separation of the fibres. This could take place as follows.

We suppose that the composite is not perfect; in particular the fibres are not perfectly straight. When a tensile stress is applied, the fibres will tend to straighten (see Fig. 16), thus applying a stress, $\sigma_{2m}$, normal to the applied stress.

If we use data from pultrusions we can estimate this normal stress, for an applied stress, $\sigma_1$, of 0.92 GPa. (This was the maximum stress used for $R = 0.1$ for the determination of $H$, flexural modulus and Poisson's ratio for the EPON 815 family of composites.) Using the previous terminology [6], the matrix stress, at the antinodes (e.g. A and B, Fig. 16) is related to the fibre stress, $\sigma_f$:

$$\sigma_{2m} = (\pi^3 a/2\lambda^2)\,\sigma_f \qquad (1)$$

where $\lambda$ is the wavelength assumed by the fibre centreline divided by the fibre diameter, and $a$ is the corresponding amplitude divided by diameter. For pultrusions of the type used here, $\lambda \simeq 43$ and $a \simeq 4$ [6]. Because

$$\sigma_f = E_f\sigma_1/E_1 \qquad (2)$$

where $E_1$ is the composite modulus in the fibre direction, equal to about 110 GPa, and $E_f$ is the fibre modulus, i.e. 228 GPa, the fibre stress is about 1.84 GPa for a 0.92 GPa applied stress. Hence, substituting the values into Equation 1, $\sigma_{2m}$ comes to about 60 MPa. This will be a tensile stress on the upper side of the fibre at A and the lower side of the fibre at B.

A cyclic strain of 0.6% is considered to be large enough to cause fatigue failure of an epoxy composite [3]; the corresponding maximum stress in the epoxy would be in the region of 60 MPa. If the epoxy were to

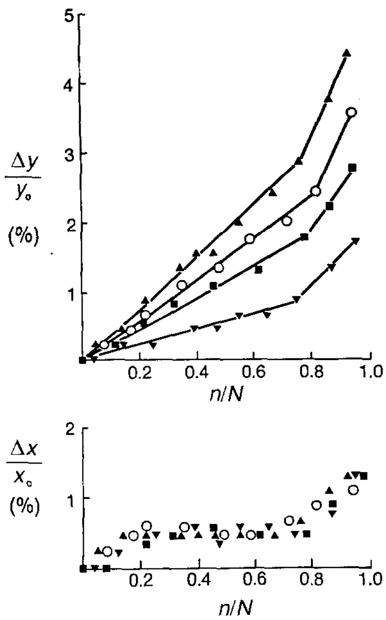


*Figure 8* Change in hole size during fatigue; top, transverse, and bottom, normal to fibre direction, $R = 0.1$. (○) E815, no additive, 550 MPa; (■) E815, 10% TMSOC, 620 MPa; (▼) D332, 15% DNSOC, 500 MPa; (▲) E828, 20% DMF, 500 MPa.

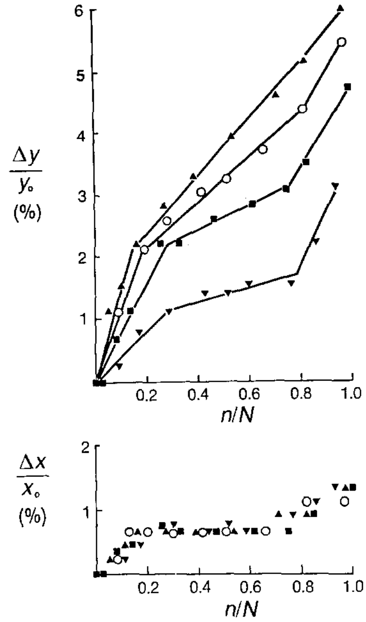


*Figure 9* Change in hole size during fatigue; top, transverse, and bottom, normal to fibre direction, $R = -0.3$. (○) E815, no additive, 670 MPa; (□) E815, 10% TMSOC, 530 MPa; (▼) D332, 15% DNSOC, 420 MPa, (▲) E828, 20% DMF, 420 MPa.

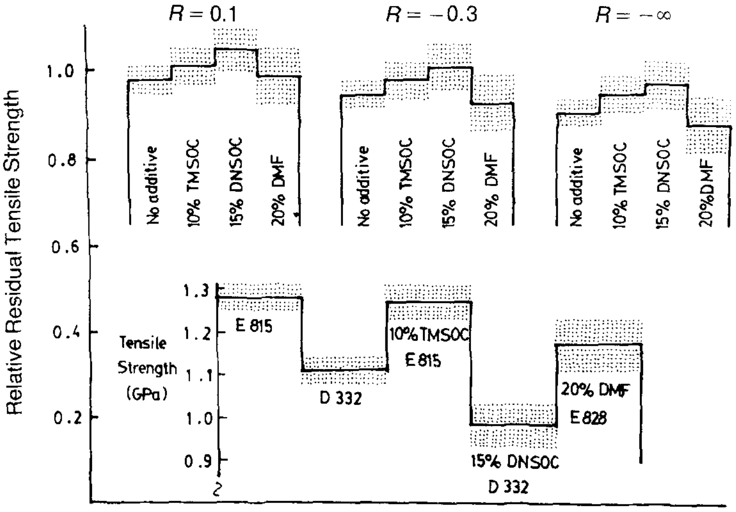


*Figure 10* Relative residual tensile strengths at about half the fatigue life, with inset the initial tensile strengths.

crack and small pieces were to be produced, they could interfere with the oscillatory motion of the fibres, lodge under the antinodes, and hence increase $a$. This could be a cause of the opening up of the holes that was observed. Also, the motion of the minute pieces of polymer could cause the observed increase in Poisson's ratio. This would also account for the increase in energy absorbed during the cycling.

The loss of integrity of the matrix could also explain the decrease in flexural modulus. The lack of significant change in the shear strength may not be a serious difficulty. This could instead indicate that the extra sinuosity of the fibres must be cancelling out the loss of matrix strength. (In shear failure, misaligned fibres will tend to intersect the plane of shear failure, and will increase the resistance of the composite to that failure.)

The cure shrinkage stress might at first sight appear to be beneficial, because it implies that the stress cycles from −20 to 40 MPa instead of 0 to 60 MPa for a typical cure shrinkage pressure of 20 MPa. However, there will be a corresponding hoop stress around the circumference of each fibre, which is tensile and amounts to about twice the magnitude of the radial shrinkage stress. (These stresses were estimated from Poisson's shrinkage, but the analysis [7] is valid also for cure shrinkage, with minor modifications.) Thus the polymer will be subject to triaxial tensile stresses, with all components greater than 20 MPa for at least part of the stress cycle, in regions close to the antinodes A, B, etc. Such triaxial stresses will strongly assist matrix cracking. Reducing the cure shrinkage stresses by using expanding monomers thus reduces the triaxial stress, and hence can be expected to reduce the rate of damage growth.

When adhesion is poor, as in the case of the silicone-coated fibres, the damage will be concentrated at the interface. The high tensile stresses generated at the interface will promote early failure there. Even with good bonding, however, interface failure can be expected to occur to some extent at least, since the interface is likely to be prone to fatigue failure at the high stresses involved.

Evidence in support of this type of damage comes from micrographic observations. Interface failure and matrix fragmentation were observed [2]. The fragmentation was particularly notable with the plasticized resin matrix, but was present in all cases.

When compressive stresses are involved ($R = -0.3$ and $R = -\infty$) the tendency for matrix splitting is much enhanced [6]; this probably accounts for the reduced fatigue life in these cases.

With laminates, such as the cross-ply laminates which have been much investigated [4], the same processes are likely to be involved in the eventual failure of the plies aligned along the direction of the stress, once the cross-plies are fully fractured. However, plies in other directions than the direction of the applied stress can help to keep the composite together during the fragmentation process described above, and so prolong the fatigue life [4].

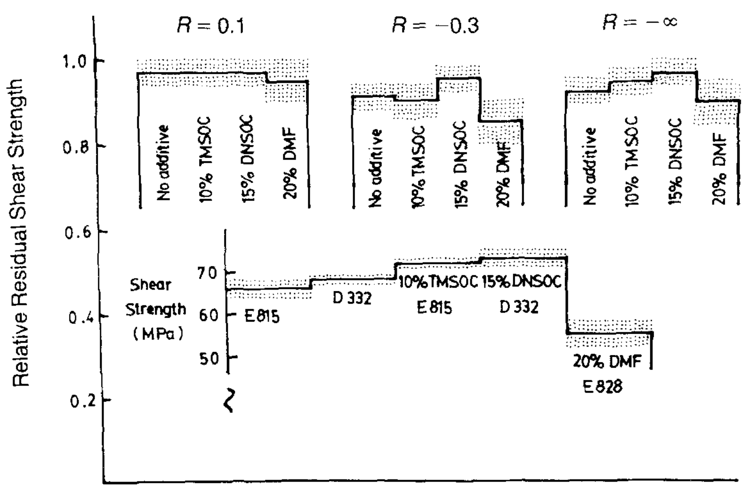


*Figure 11* Relative residual shear strengths at about half the fatigue life, with inset the initial shear strengths.

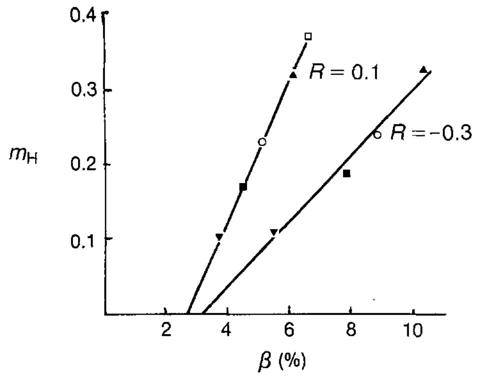


*Figure 12* Rate of increase of hysteresis loop energy plotted against the slope of the *S–N* curve. (○) E815, no addition; (■) E815, 10% TMSOC; (▼) D332, 15% DNSOC; (▲) E828, 20% DMF; (□) E815, silicone.

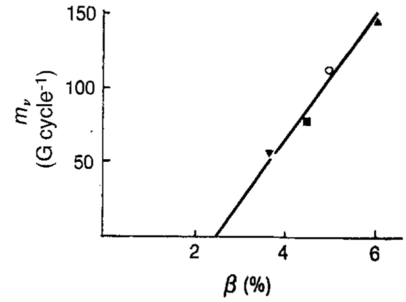


*Figure 15* Rate of increase of Poisson's ratio plotted against the slope of the *S–N* curve, $R = 0.1$. For key, see Fig. 13.

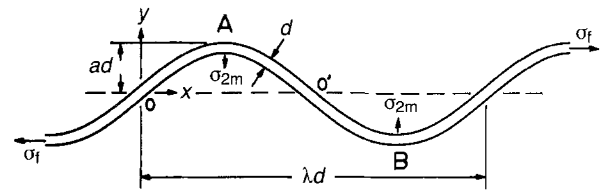


*Figure 16* Schematic drawing of imperfectly aligned fibre: misalignment in the form of a sine wave. Stress applied in the *x*-direction.

## 5. Conclusions

Damage appears to develop continuously during the fatigue of aligned fibre composites. Thus holes grow in size, the energy absorbed from the applied force increases, the flexural modulus decreases and the Poisson's ratio increases. The damage probably originates at imperfections in the composite, such as lack of perfect straightness of the fibres. This could be causing the gradual cracking and eventual fragmentation of the matrix due to off-axis stresses induced by the fibre curvature. Fragments of matrix could interfere with the oscillatory motion of the fibres, and start the separation of the fibres which must accompany the increase in size of the pre-existing holes used in some of the tests, and cause the apparent Poisson's ratio increase, perhaps by increasing the amplitude of the oscillatory motion of the fibres.

The rate of damage growth is reduced by reducing the microstresses that exist in the composite. This can be achieved by using expanding monomers, in thermoset systems at least. When fatigue involves compressive stresses, matrix damage rates are greater, probably due to the greater tendency for the composite to split. Here reducing the shrinkage stresses has a more beneficial effect.

Laminates probably fail in much the same way as do aligned fibre composites, but laminae which are oblique to the stresses fail before the axial laminae, and the cracks produced could well accelerate the damage growth observed here. Otherwise, however, the failure in the plies aligned in the stress direction is expected to follow the sequence described here; i.e. slight misalignments giving rise to transverse stresses which fatigue the polymer (and the interface), produce tiny matrix fragments which interfere with the fibres and eventually cause them to break.

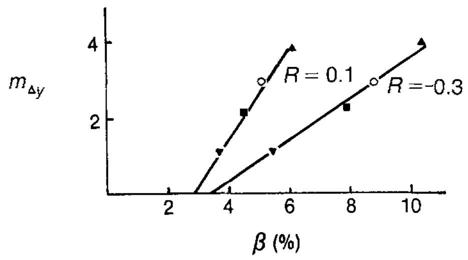


*Figure 13* Rate of increase in hole size plotted against the slope of the *S–N* curve. (○) E815, no additive; (■) E815, 10% TMSOC; (▼) D332, 15% DNSOC; (▲) E828, 20% DMF.

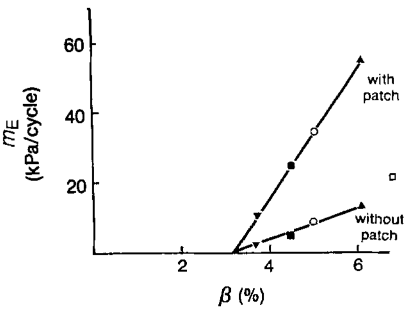


*Figure 14* Rate of loss of flexural modulus plotted against the slope of *S–N* curve, $R = 0.1$. For key, see Fig. 12.

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