JOURNAL OF MATERIALS SCIENCE 24 (1989) 4427–4431

The durability of controlled matrix shrinkage composites

Part 2 *Properties of carbon fibre-epoxy copolymer pultrusions*

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

Tension–tension ($R = 0.1$) tension–compression ($R = -0.3$) and zero-compression ($R = -\infty$) fatigue tests have been carried out on pultrusions made with epoxy copolymers with expanding monomers, and epoxies containing a non-reactive diluent. In addition some fibres were coated with silicone oil to reduce their adhesion to the matrix before being used to make the pultrusions. Reducing the resin shrinkage increased the fatigue endurance, as long as the interfacial adhesion was not reduced. The results suggest that for unidirectional composites, lack of perfect fibre straightness may be a major factor contributing to interface and matrix fatigue, which then leads to progressive fibre failure which is the ultimate cause of composite failure.

1. Introduction

In the first paper of this series [1], it was shown that the use of expanding monomers reduced internal stresses and improved the across-the-grain toughness of carbon fibre pultrusions without any loss of shear strength. Adding a plasticizer (dimethyl formamide, DMF), on the other hand, while reducing internal stresses appeared to have no beneficial effect on composite toughness and caused a marked loss in shear strength.

The fatigue properties of carbon fibre composites are important because of their widespread and increasing use in aerospace. A great deal of work has been carried out on damage processes in laminates, where a number of different matrix failure processes have been documented [2]. In the case of aligned fibre composites, failure mechanisms have also been identified [3]. However, the use of expanding monomers, which provides the opportunity of controlling a hitherto uncontrollable variable, i.e. the polymer shrinkage stress, can be expected to cast new light upon these failure processes.

This paper describes some experiments on the fatigue of controlled resin shrinkage composites, and for comparison, some composites in which the resin was plasticized with DMF, and some composites in which the fibres were coated with silicone fluid before being used to make the composites.

2. Experimental method

Pultrusions were made using Hercules ASi carbon fibres resins with additives of different amounts of two different expanding monomers, i.e. dinorbornene spiro orthocarbonate (DNSOC), and tetramethyl spiro orthocarbonate (TMSOC). Composites were also made with the DMF added to the resin. In addition, a composite was made with fibres coated with DOW Corning DC 20 silicone fluid from an acetone solution. After coating, the fibres were dried for 2 h at 60° C. The structure of the monomers, the curing conditions and the techniques used for manufacturing the same are all described in the previous paper [1]. The fibre volume fraction was about 0.5.

For the fatigue tests samples were first proof tested in order to screen out weak ones. (This has been shown to reduce the scatter in the results [4]). For this, the specimens were preloaded to 80% of their mean ultimate tensile strength. Those that survived without fracturing were used for the fatigue tests. A few were retested to check whether the proof testing resulted in any change in tensile strength and Young's modulus, and no significant change was noted.

For the tests the specimens were end tabbed with aluminium $38.1 \times 25.4\,mm^2$ and 3 mm thick, bonded with epoxy. The gauge length was 25.4 mm. They were tested in an MTS servohydraulic machine, with hydraulic grips. The grip pressure was adjusted so that the specimen did not slip, yet was not damaged by the grips, following recommendations supplied by MTS. They were tested at constant load amplitude at stress ratios R (i.e. minimum stress/maximum stress) of 0.1 (tension–tension), -0.3 (tension–compression) and $-\infty$ (zero-compression). A frequency of 10 Hz was used except for the low cycle fatigue tests (lives < 1000 cycles). For these a frequency of 2 Hz was used to avoid significant heating of the specimens. For each stress ratio, fatigue tests were carried out at four stress levels, with five replicate tests at each stress level. The specimens were fatigued until final failure occurred.

3. Experimental results

Figure 1 shows a typical fatigue curve for a stress ratio, $R = 0.1$. The triangles represent the static tensile strengths. The centre line represents the mean life,

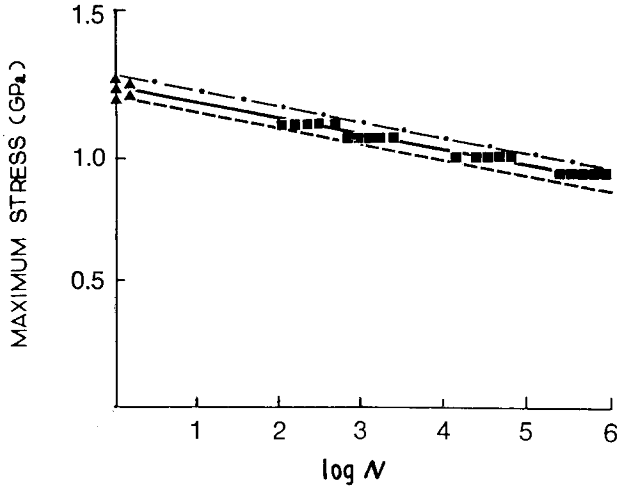

Figure 1 Fatigue results for carbon–epoxy (EPON 815) pultrusions. $R = 0.1$. The upper and lower lines indicate 0.98 and 0.02 failure probabilities.

while the upper and lower lines represent 0.98 and 0.02 failure probabilities, respectively. These lines were obtained by statistical analysis [5]. A two-parameter Weibull distribution was used for pooling the data, and the pooled fatigue lives are shown in Fig. 2, for an S–N curve represented by the equation.

$$S_{\max} = KN_0 - 1/b \qquad (1)$$

Here $S_{\max}$ is the failure stress, N_0 is the mean time to failure at the stress, and K and b are constants representing material properties.

The fatigue curve at $R = -0.3$, appeared to have a steeper slope when the tensile strength was used for the static result, Fig. 3. However, this approach, and using the two parameter Weibull distribution as for the $R = 0.1$ case, gave a linear least square line (centre line in Fig. 3) that did not fit the results at 0.84 and 0.58 GPa very well. Instead, extrapolation of the mean stress to a static value of 1.18 GPa, with corresponding changes to the upper and lower limits, Fig. 4, gave better agreement. The slope of the lines in Fig. 4 is still somewhat greater than that for $R = 0.1$ (Fig. 1).

In the case of the wholly compression fatigue tests, the results were not well behaved, Fig. 5. The fatigue results at a minimum stress of -620 MPa (i.e. a maximum compression stress of 620 MPa) were significantly below the line joining the fatigue results and the static compression strength.

The material constant K (Equation 1) was a little greater than the static tensile strength (UTS) for the tensile fatigue tests, Fig. 6. In the case of the tension–compression results ($R = -0.3$) the discrepancy was larger, as also shown in Fig. 6. The $R = 0.1$ results fitted the line drawn, i.e.

$$\text{UTS} = 0.95\,K \qquad (2)$$

within the margin of error in most cases.

The other material constant, b, correlated with the slope of the S–N curve. If β is defined as the slope, % loss in strength per decade, for an S–N curve plotted in the usual way, i.e. stress amplitude on a linear scale and number of cycles to failure, N, on a logarithmic scale, then β correlates with b as shown in Fig. 7. The

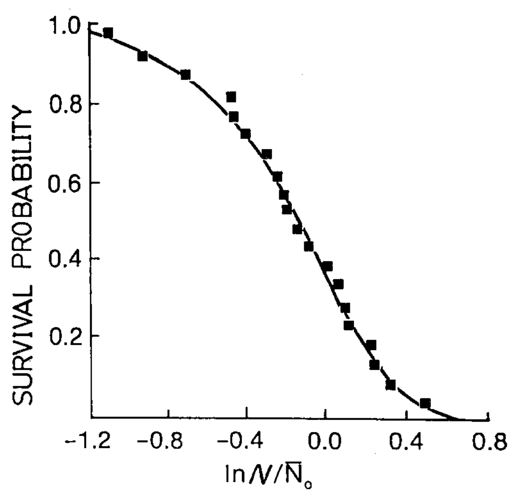

Figure 2 Pooled fatigue life curve for specimens giving results shown in Fig. 1.

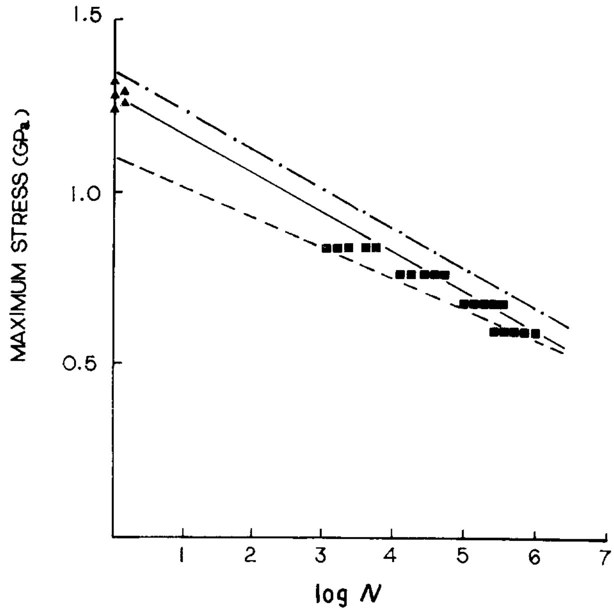

Figure 3 Fatigue results for carbon–epoxy (EPON 815) pultrusions. $R = -0.3$. The upper and lower lines indicate 0.98 and 0.02 failure probabilities.

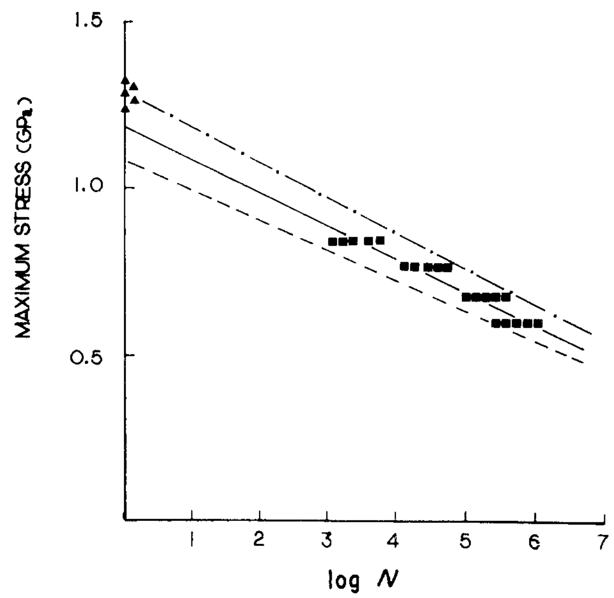

Figure 4 Results in Fig. 3 with failure probability lines adjusted. $R = -0.3$.

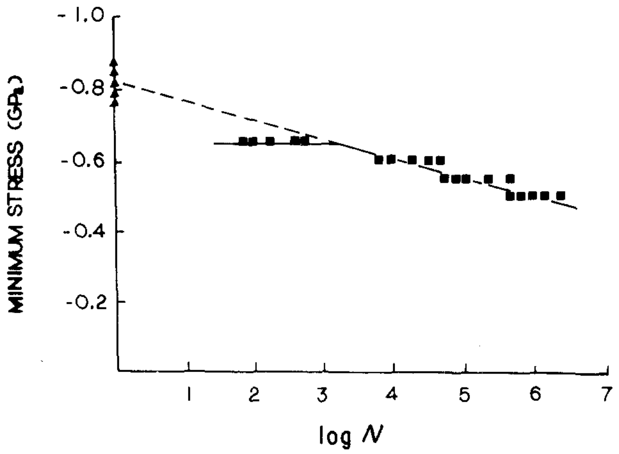

Figure 5 Fatigue results for carbon–epoxy (EPON 815) pultrusions. $R = -\infty$.

results for both $R = 0.1$ and $R = -0.3$ fit quite well the line drawn on the graph, which is given by

$$\beta = 2 + 100/b \qquad (3)$$

In the case of the DER 332 epoxy – DNSOC copolymer composites the fatigue endurance appeared to be improved when the shrinkage stress was reduced, Fig. 8. (The shrinkage stress was controlled by the amount of DNSOC added to the epoxy–hardener mixture.) The effect appeared to be approximately linear with shrinkage stress; for a change in shrinkage stress of about 20 MPa, β decreased by 2% per decade (i.e. from 5.4% to about 3.4%) for $R = 0.1$. The decrease in β was greater for $R = -0.3$, i.e. 4% per decrease (from 9 to 5%). The other spiro, TMSOC, did not give a very significant reduction in β, Fig. 9. Both the use of DMF, and the silicone coating of the fibres increased β substantially, see Fig. 9. In compression fatigue ($R = -\infty$) the slopes of the S–N curves were less than for tension-compression ($R = -0.3$) except for the EPON 828–DMF, which

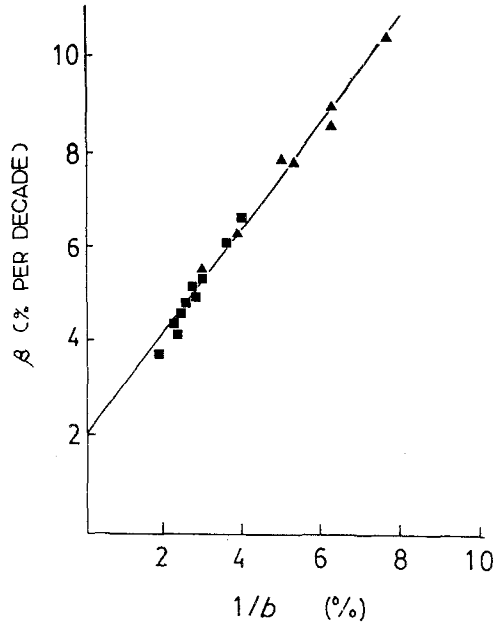

Figure 7 Slopes of S–N curve against materials parameter for (■) $R = 0.1$, and (▲) $R = -0.3$.

was almost identical; compare Figs 9 and 10. There was again some reduction in β as the polymer shrinkage stress was reduced. (Note: all the fatigue tests for $R = -\infty$ gave anomalously low results in the low cycle fatigue range.)

Specimens removed from the MTS machine during the experiments, and examined in the SEM, displayed quite severe damage, especially when compression was involved in the fatigue test. Fig. 11a shows fibre kinks and breaks which were observed at about half the fatigue life ($N/N_0 = 0.55$; N is the number of cycles at which the specimen was removed for SEM examination) for $R = -0.3$, with DER 332–15% DNSOC. With DMF, under the same conditions, fibre debonds and breaks were observed instead, together with

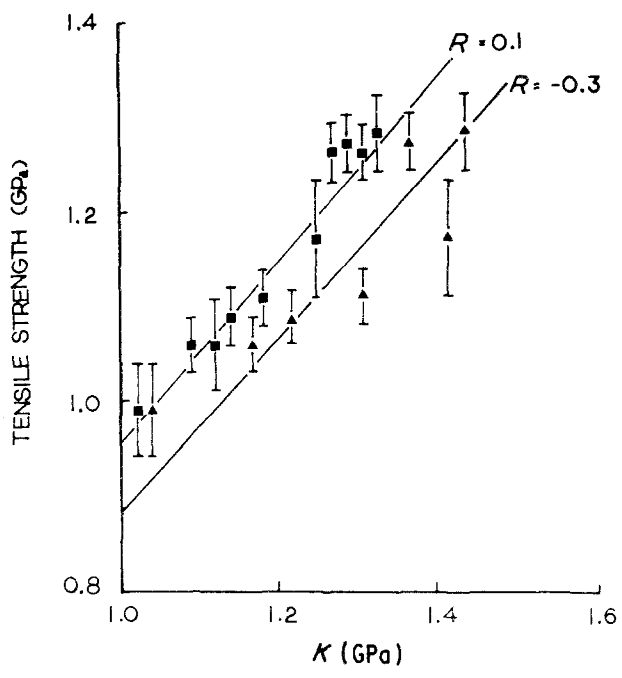

Figure 6 Tensile strength against materials parameters given in equation 1.

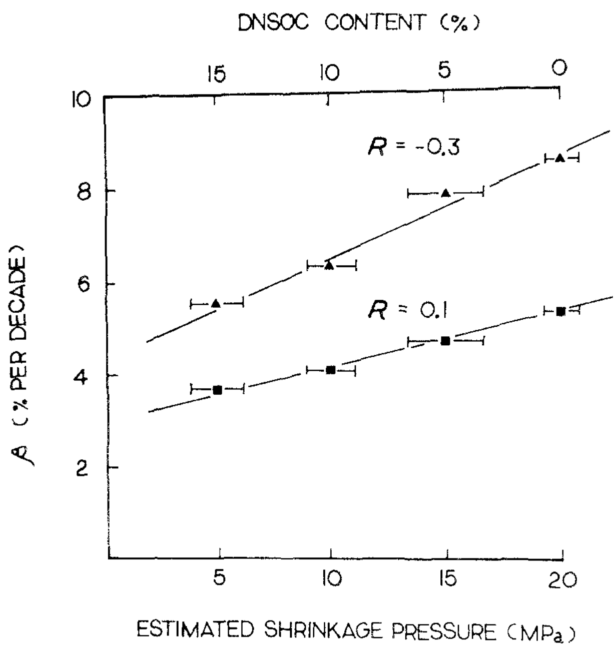

Figure 8 Slopes of S–N curves against polymer cure shrinkage stress for DER–DNSOC matrices. (Note: the result for EPON 815–10% DNSOC was barely distinguishable from that for DER 332–10% DNSOC).

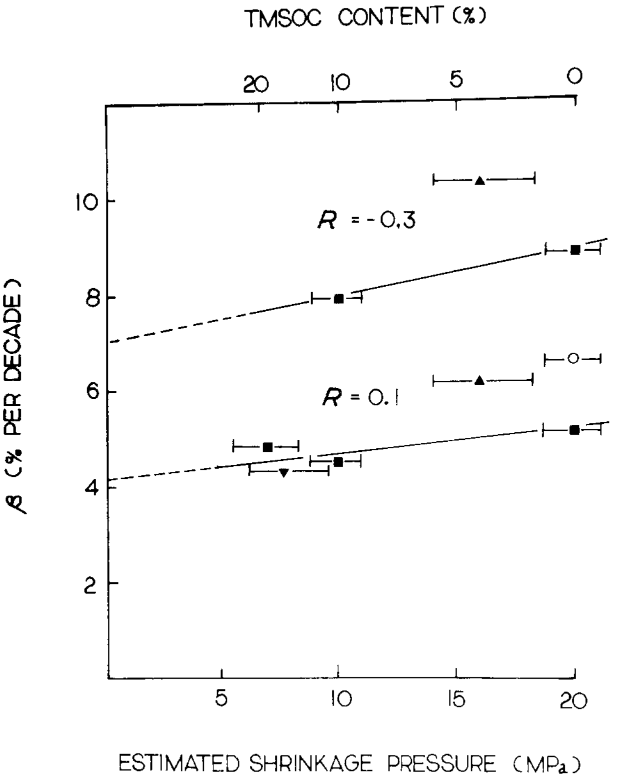

Figure 9 Slopes of *S–N* curves against polymer cure shrinkage stress (TMSOC content values only refer to EPON 815–TMSOC results). (■) EPON 815–TMSOC; (▾) EPON 815–10% DNSOC; (▴) EPON 828–20% DMF; (○) silicone coated fibres (EPON 815).

considerable matrix cracking, Fig. 11b. In tension–tension fatigue fibre debonding, Fig. 12a, and matrix cracking, Fig. 12b were observed. At final fracture, Fig. 12c, broken fibres could be observed with little matrix adhering to them, and the matrix was also broken into small pieces.

The failure mode was affected by the stress ratio. For $R = 0.1$, mainly splitting or broom-like failure was observed, while for $R = -0.3$ buckling as well as splitting occurred, and for $R = -\infty$ failure was normally by buckling.

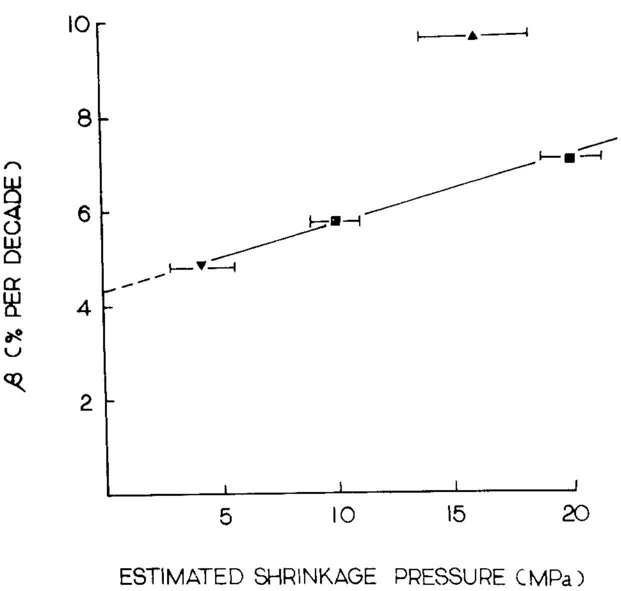

Figure 10 Slopes of *S–N* curves against polymer cure shrinkage stress: compression fatigue ($R = -\infty$). (■) EPON 815–TMSOC; (▾) DER 332–15% DNSOC; (▴) EPON 828–20% DMF.

4. Discussion

The statistical analysis used gave good results with $R = 0.1$. However, it could not be used for $R = -0.3$ because the static stress is not the appropriate value to use for the value on the ordinate. In the case of the compression test the higher compressive stresses gave anomalously short fatigue lives. This could well have been due to premature buckling, despite the short (25.4 mm) specimens used for this test. The buckling could have developed after the matrix became damaged due to off-axis stresses arising from imperfections, such as lack of fibre straightness. Clearly some alternative approach, e.g. shorter specimens (too short to buckle) is necessary. In what follows the results at higher compressive stresses will not be included.

The results with the DNSOC strongly suggest that with aligned fibre pultrusions the shrinkage stresses have an important effect on fatigue. Unfortunately their complete removal (as indicated by the extrapolations to the ordinate in Fig. 8) does not altogether prevent the fatigue process occurring. Other factors, such as composite imperfections (e.g lack of straightness of fibres and voids) probably play a part also.

The fibre–matrix bond strength also plays an important role in fatigue, even when the stresses are always tensile, since coating the fibres with silicone increases β by some 30% (see Fig. 9). The composites made with DMF also cause about a 30% increase in β compared with the interpolated value for the same estimated shrinkage stress using DNSOC (Fig. 8). Since the micrograph (Fig. 11) indicates loss of adhesion in the case of the DMF, and the DMF reduced the shear strength by about 13% [1], it seems likely that adhesion loss was the main factor influencing the fatigue endurance in this case. Some loss in adhesion is possible in the case of the TMSOC, since there was a 5% loss in shear strength when 20% TMSOC was added to the epoxy used to make composites, as compared with the epoxy homopolymer [1]. This could partly explain the much smaller improvement in fatigue endurance given by the TMSOC (compare Figs 8 and 9). However, other factors are likely to be playing a role, since at 10% TMSOC addition, loss of shear strength was not observed: 10% TMSOC gives an estimated shrinkage stress of 10 MPa. The compression fatigue results, Fig. 10, also indicate that controlling the shrinkage improves the endurance. The effects, however, are much smaller. The 70% increase in β that is obtained in this case (Fig. 10) fits in nicely with the well documented effect of fibre–matrix adhesion on compressive strength [6].

Overall, the results suggest that there may be a strong correlation between the factors influencing fatigue and compression strength in aligned fibre pultrusions. Since pultrusions are usually imperfect from the point of view of fibre straightness, as indicated by lower than rule of mixtures moduli, in compression [7] it is likely that this particular imperfection plays a key role in fatigue. Any lack of straightness will result in stresses at right angles to the applied stress as the fibres attempt to become more straight in the tension part of the loading cycle. The opposite effect occurs during the compression part of the cycle.

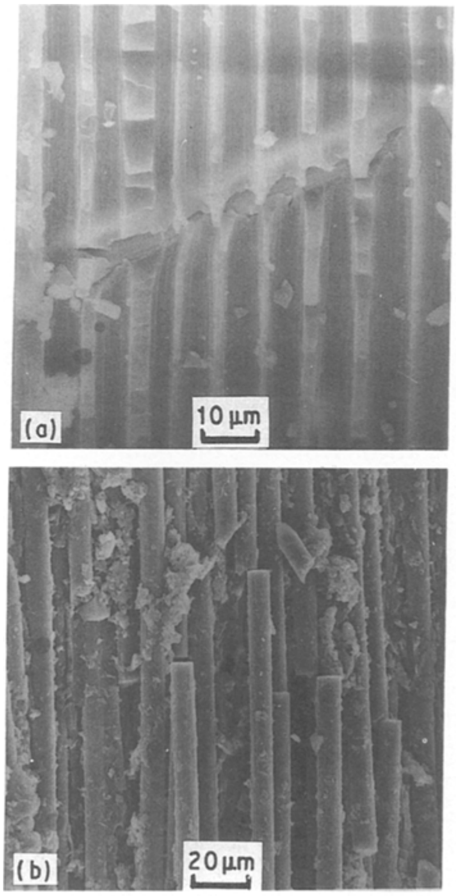

Figure 11 Damage visible at specimen surfaces at $N/N_0 = 0.55$ with $R = -0.3$. Matrices: (a) DER332–15% DNSOC; (b) EPON 828–20% DMF.

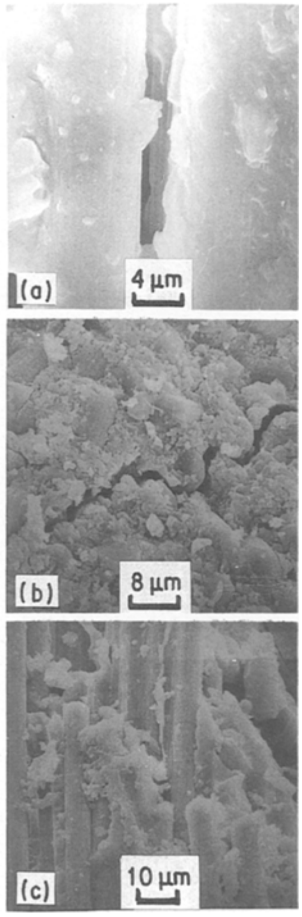

Figure 12 Damage visible at specimen surfaces with EPON 815 matrix, with $R = 0.1$, (a) $N/N_0 = 0.50$, (b) $N/N_0 = 0.60$, and (c) fracture surface at $N/N_0 = 1.0$ (i.e. final fracture).

Thus both interface and matrix are subject to cyclic stresses. Reducing the mean stress level, by using expanding monomers, is thus likely to increase the fatigue life of the interface and matrix, and hence improve the fatigue endurance of the composite. Fibre failure in the compression part of the cycle could occur once the fibre has lost the support of the matrix due to these effects. In tension–tension fatigue, fibre breakage could occur due to flexure around broken pieces of matrix. Thus the fatigue process probably involves gradual degradation of the matrix and interface until the composite has reached a level of damage at which fibre failure can occur. Fibres then break progressively until the number remaining is insufficient to support the load. This process would be assisted if microvoids were present, since these could allow microbuckling of the fibres. With unidirectional laminates, the same processes probably operate, but at a lower level, since it is very likely that laminates have straighter fibres than pultrusions.

5. Conclusions

Reducing the cure shrinkage stresses in the resin improves the fatigue endurance of a composite. It is important that the fibre–matrix bond strength is preserved, however, for the improvement to be substantial.

In pultrusions, the main fatigue processes take place in the resin, and at the fibre–matrix interface, at least initially. Once resin and interface are badly damaged, the fibres can start breaking, due to the possibility of excessive flexure of the fibres.

Acknowledgements

The authors are grateful to the Canadian Department of Defence (DREP) for support for this work.

References

1. P. W. K. LAM and M. R. PIGGOTT. Submitted to *J. Mater. Sci.*
2. K. L. REIFSNIDER and R. D. JAMISON. *Int. J. Fatigue* **4** (1982) 187.
3. R. TALREJA. *Proc. R. Soc. London* **A378** (1981) 461.
4. A. S. W. WANG, P. C. CHOU and J. ALPER. ASTM STP 723 (1981) 116.
5. J. M. WHITNEY, ASTM STP 723 (1981) 133.
6. G. M. MARTINEZ, D. M. R. BAINBRIDGE, M. R. PIGGOTT and B. HARRIS, *J. Mater. Sci.* **16** (1981) 2831.
7. M. R. PIGGOTT and B. HARRIS. *J. Mater. Sci.* **15** (1980) 2523.

Received 27 July 1988
and accepted 5 January 1989