JOURNAL OF MATERIALS SCIENCE 24 (1989) 4068–4075

The durability of controlled matrix shrinkage composites

Part I *Mechanical properties of resin matrices and their composites*

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

---

Controlled matrix shrinkage composites have resin matrices in which the cure shrinkage is controlled by adding expanding monomers to epoxy (and other) resins. The shrinkage stresses can be reduced to about one third of their normal values, accompanied by a 50% increase in impact resistance of the composites, with no corresponding loss of shear strength. Tensile and compressive properties of the composites are slightly reduced, although the resin matrices themselves have slightly improved properties as a result of the addition of the expanding monomer. In contrast to this, the addition to the resin matrix of a compatible solvent, dimethyl formamide, had very little effect on the shrinkage stress or composite impact strength but caused losses of resin properties which were manifested in a decrease in composite shear strength.

---

1. Introduction

Carbon fibre reinforced epoxies are widely used in the aerospace industry because of their excellent mechanical properties and their light weight. However, they lack ductility, and their resistance to fracture is small. Some increase in toughness across the grain is possible if the cure shrinkage of the matrix is reduced [1]. This can be effected by the use of expanding monomers, and preliminary work with spiro ortho carbonates indicates that a substantial increase in toughness is possible [2]. In these experiments dinorbornene spiro ortho carbonate, copolymerized with epoxy, was used as the matrix for carbon fibre pultrusions. The increase in toughness was effected without loss of other properties. The resins, and composites made therefrom, were slightly more water resistant than the corresponding specimens made with epoxy homopolymers [3, 4].

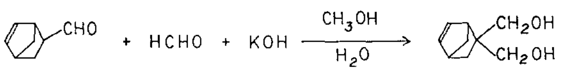
In this series of papers a more thorough going examination of the properties of these controlled matrix shrinkage composites is described. In particular, the durability will be examined, and indicators of damage during fatigue will be monitored. This first paper describes composite fabrication techniques and static properties.

2. Experimental details

2.1. Materials and specimen preparation

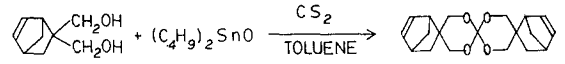
Three different epoxy resin systems, based on commercial DGEBA epoxies, were used for the experiments. These were: (1) Dow DER 332, to which was added dinorbornene spiro ortho carbonate (DNSOC), (2) Shell EPON 815 (which contains the reactive diluent butyl glycidyl ether to reduce the viscosity) to which was added tetramethyl spiro ortho carbonate (TMSOC); and (3) Shell EPON 828, to which was added a non-reactive swelling agent, dimethyl formamide (DMF).

The spiros were synthesized in the laboratory. The DNSOC was prepared from 5-norbornene-2-carboxaldehyde in two stages. The formaldehyde (37% aqueous solution) in a methanolic potassium hydroxide solution was first reacted to produce the diol



(1)

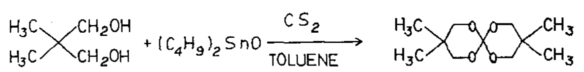
The product was identified using proton magnetic resonance (PMR) and IR spectra. It had a melting point of 115.2 ± 0.7° C. The diol was then reacted with dibutyltin oxide in anhydrous toluene, in the presence of a two-fold excess of carbon disulphide



(2)

The spiro was identified using PMR and IR spectra, and had a melting point of 242.9 ± 0.6° C.

The TMSOC was prepared directly from the appropriate diol (2.2-dimethyl-1,3-propanediol) using the same reaction as above



(3)

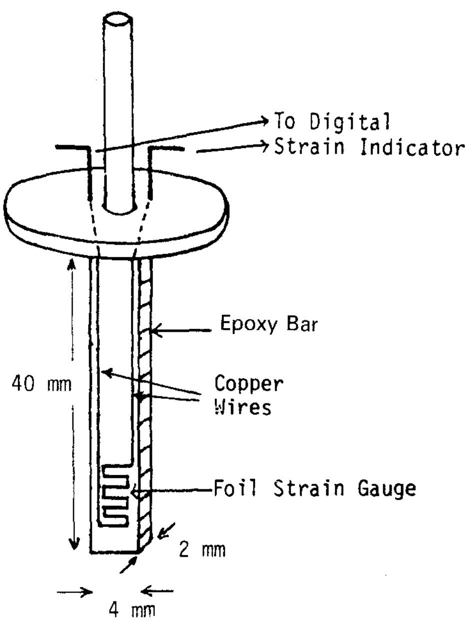
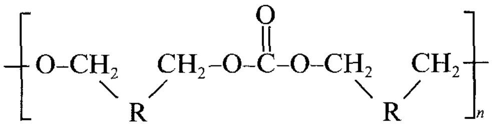


Figure 1 Shrinkage strain measurement: probe used.

It was also identified using PMR and IR spectra. Its melting point was 138.3 ± 0.7 °C.

The spiros, when polymerized in anhydrous dichloroethane under dry nitrogen at 80° C, in the presence of a trace of Anchor 1171 BF_3-amine complex produced the polyoxycarbonates having the structure



where R represents, norbornene for the DNSOC, and $C(CH_3)_2$ for the TMSOC. The melting points of the polymers were 168.5 ± 1.5° C (from DNSOC) and 123 ± 2° C (from TMSOC). Polymerization was confirmed by the appearance of the C=O absorption in the IR spectrum at $1740\,cm^{-1}$.

Carbon fibre pultrusions were made by soaking Hercules AS1 carbon fibres in the vacuum degassed resin–additive–hardener mixtures, and then pulling them inside aluminium moulds 300 mm long with 3.0 mm × 20.0 mm cross-sections. They were oven cured as indicated in Table I, which also shows the hardeners used. Samples without fibres were made by casting the resin mixtures in silicone moulds, which produced dogbone and oblong shaped specimens, sized appropriately for the different tests.

For some tests the carbon fibres were soaked in a 5% solution of silicone oil (DOW DC 20) in acetone and allowed to dry. The process was repeated two more times to ensure thorough wetting of the fibres by the silicone. After drying in a vacuum oven at 60° C for 2 h these fibres were used to produce pultrusions, as described above. Fibre volume fractions (V_f) were about 0.5 for all tests except the Izod test, for which they were 0.4.

Shrinkage measurements were carried out on the resins using a specially constructed probe, as shown in Fig. 1. This had strain gauges attached to it, and was just big enough to accommodate them. It was coated with fluorocarbon release agent (so that it could be removed from the cured resin and reused) and connected to a digital microstrain indicator (Vishay-Ellis digital model 20) via a dummy probe for temperature compensation (see Fig. 1). The shrinkage stresses were measured on resins as they cured at room temperature. Prior to insertion of the probe in the resin, the polymerization of the mixture was initiated at 60° C, and the resin was then cooled to room temperature.

The densities of the cured resins were measured using the pyknometer method (ASTM D-792-66). Their surfaces were polished prior to immersion in the liquid medium (distilled water) to prevent the retention of air bubbles on the surfaces.

For the measurement of T_g of the TMSOC, the monomer was polymerized in solution in anhydrous toluene with 1% Anchor 1115 at 111°C in reflux. A Du Pont TMA (Model 990) with DSC cell was used for the heat scan of the precipitated powder, at $10°C\,min^{-1}$.

2.2. Mechanical testing

The tensile and compressive tests on the cured resins were carried out on a screw Instron (Model TT) at a cross head speed of $1.0\,mm\,min^{-1}$. Compression specimens were 12.7 × 12.7 × $25.4\,mm^3$, except for the modulus measurements, for which the lengths were twice as great (50.8 mm), while the tensile specimens, gauge length 65 mm, width 13 mm and thickness 3 mm, conformed to ASTM D-638-80. Flexural tests were carried out on 3 mm thick specimens, 13 mm wide with a span to depth ratio of 16 : 1 at the same cross-head speed.

For the tensile and compressive tests on the unidirectional fibre composites an MTS servohydraulic machine was used at a testing rate of $0.1\,kN\,s^{-1}$. The tensile specimens were end tabbed with aluminium 38.1 × $25.4\,mm^2$ and 3 mm thick, bonded with epoxy. They had a gauge length of 25.4 mm for strength measurement and 76.2 mm (to accommodate the extensometer) for the estimation of Young's modulus.

TABLE I Curing data for controlled contraction matrices

Epoxy	Controlled contraction modifier	Curing agent	Curing cycle	
			Temperature (°C)	Time (h)
EPON 815	Tetramethyl spiro orthocarbonate (TMSOC)	2.5% Anchor 1171 10% TETA	60 120	4 16
EPON 828	N, N-dimethyl formamide (DMF)	15% TETA	60 100	4 16
DER 332	Dinorbornene spiro orthocarbonate (DNSOC)	7% Anchor 1115	80 135	2 30

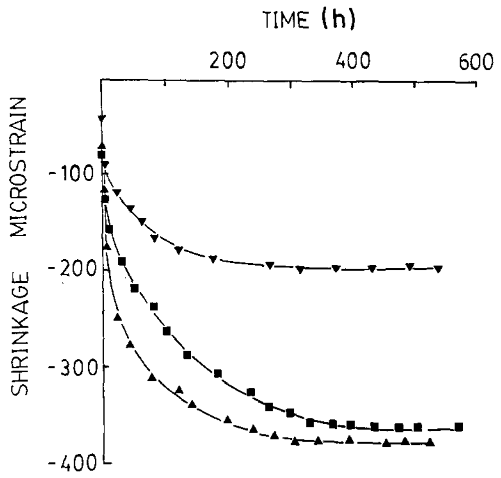


Figure 2 Curing strains plotted against time for resins cured at room temperature. (▼ DER 332-10% DNSOC, ■ EPON 828-20% DMF, ▲ DER 332).

For the compression tests the end confinement technique was used: the specimens were fitted snugly into slots 5 mm deep. They were $20.0 \times 3.0\,\mathrm{mm}^2$ with 10 mm gauge lengths.

Flexural and short beam shear tests were carried out on the Instron at $1.0\,\mathrm{mm\,min}^{-1}$ with span to depth ratios respectively of 16 : 1 and 5 : 1 (ASTM D2344). The impact strengths were measured using a Tinius Olsen Impact Tester according to ASTM D256A with allowance made for windage and friction. A slight deviation from the ASTM specification concerned the notch depth. In order to achieve fracture rather than delamination, the notch depth used was at least half the specimen thickness.

For all mechanical properties five replicate tests were carried out. Results are plotted as means with error bars representing ± 1 standard deviation. The absence of an error bar indicates that two standard deviations were encompassed by the symbol indicating the result.

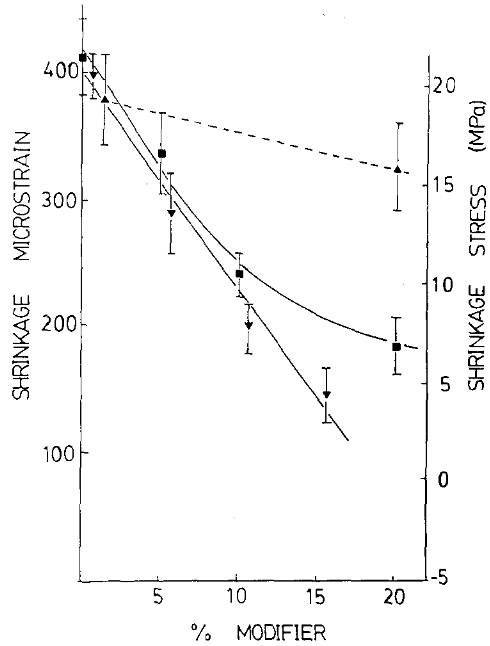


Figure 3 Curing strains and stresses plotted against amount of modifier for resins cured at room temperature. (▲ EPON 828-DMF, ■ EPON 815-TMSOC, ▼ DER 332-DNSOC).

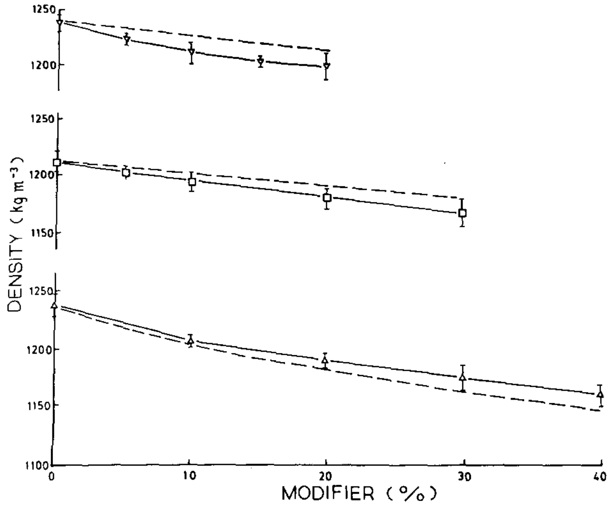


Figure 4 Densities plotted against amount of modifier for resins cured at room temperature. Broken lines are mixture rule (Equation 4). (▽ DER-DNSOC, □ EPON 815-TMSOC, △ EPON 828-DMF).

3. Experimental results

Fig. 2 shows the shrinkage strains as a function of time for three of the resin matrices. At room temperature, the strains took 400 to 600 hours to develop fully. The effect of the DNSOC was to reduce the shrinkage to about one third that of the epoxy homopolymer. The DMF had very little effect. This can be seen more clearly in Fig. 3 where the strains are plotted as a function of the amount of modifier (DNSOC, TMSOC and DMF). The corresponding stresses are estimated on the basis of the epoxy homopolymer giving a stress of about 20 MPa [4]. The densities are shown in Fig. 4. The curves labelled 'calculated' are estimated on a rule of mixtures basis

$$\varrho_{\mathrm{ccm}} = \varrho_{\mathrm{e}}\varrho_{\mathrm{a}}/[\varrho_{\mathrm{a}} + (\varrho_{\mathrm{e}} - \varrho_{\mathrm{a}})W_{\mathrm{a}}] \qquad (4)$$

where ϱ_{ccm}, ϱ_{e} and ϱ_{a} are the densities of the controlled contraction matrix, the cured epoxy resin, and the additive respectively, and W_{a} is the weight fraction of the additive.

At small additions (5 to 10%) both spiros increased the tensile strength of the resins to a small extent, Fig. 5, while the Young's modulus was not affected

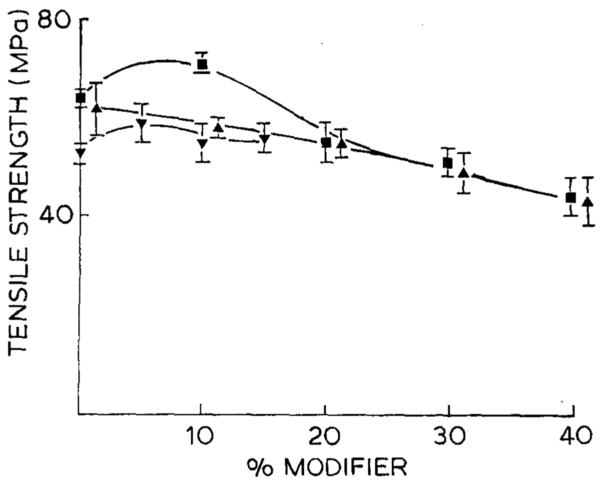


Figure 5 Tensile strengths of fully cured resins plotted against amount of modifier. (■ EPON 815-TMSOC, ▼ DER 332-DNSOC, ▲ EPON 828-DMF).

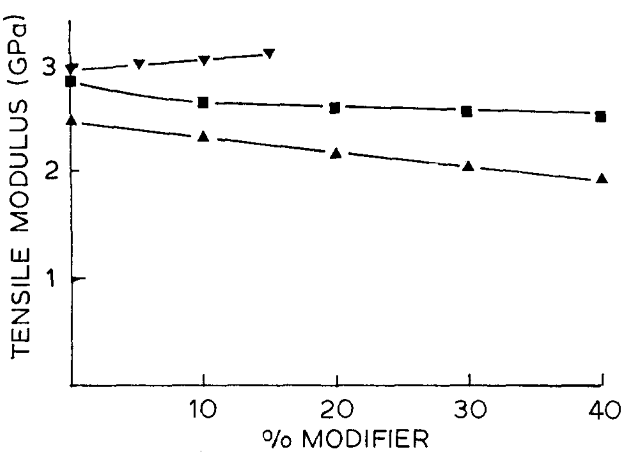


Figure 6 Young's moduli of fully cured resins plotted against amount of modifier. (▼ DER 332-DNSOC, ■ EPON 815-TMSOC, ▲ EPON 828-DMF).

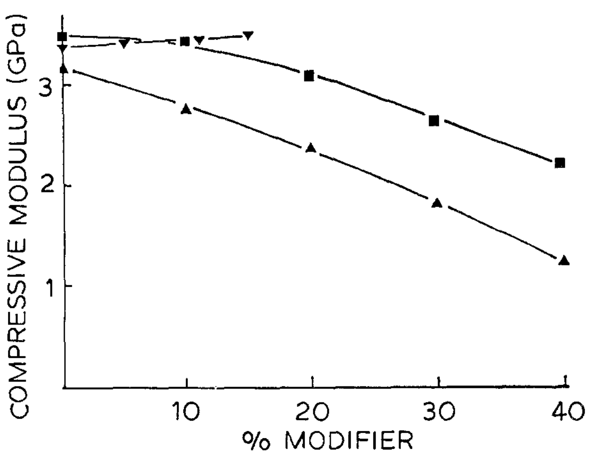


Figure 8 Compressive moduli of fully cured resins plotted against amount of modifier. (Symbols as Fig. 6).

very much, Fig. 6. With more than 10% of modifier, however, the tensile properties declined, and with DMF the tensile properties were reduced at all concentrations. No more than 15% of DNSOC was added to the epoxy because it was only moderately soluble, even at 100° C. The trends in compressive properties are similar, Figs. 7 and 8. The tensile stress–strain curves, Fig. 9, indicated that the EPONs had a little more ductility than the DER. The DNSOC marginally reduced the breaking strain of the DER, and the TMSOC and DMF increased the breaking strain of the EPONs slightly. The flexural strengths of the resins containing DMF could not be measured because the pultrusions were highly flexible and could not be induced to fail with the span to depth ratio used. The other modified resins had flexural strengths which reflected the compressive rather than tensile strengths, Fig. 10.

The tensile and compressive properties of the composites were not much affected by the matrices, see Table II, though there was some significant loss in tensile strength in the case of the composites made with resins containing 10 and 15% of DNSOC, and a loss in compressive strength with the resins which had DMF, and with the silicone coated fibres. The composites with the higher compressive strengths failed by transverse fracture, with very little evidence of in-plane fracture. However, with the others, compressive failure was accompanied by extensive delamination (silicone coated fibres) and kinking (DMF).

The DNSOC did not significantly affect the flexural strength or modulus of the composites, Figs 11 and 12, but other additives caused decreases in both flexural strength and modulus. The mode of failure was changed, as well. The unmodified epoxies and the epoxies containing DNSOC failed on the tensile side of the specimen, initially. With increasing amounts of TMSOC or DMF, however, there was an increasing tendency towards failure being initiated in compression. In the case of the shear strength, the DNSOC caused a small increase, while both TMSOC and DMF gave an initial increase at small concentrations, and a progressive decline at larger amounts, Fig. 13. The silicone coated fibres gave composites with the lowest shear strengths (38 ± 2 MPa; see Fig. 14) and transverse tensile strengths, σ_{2u} (43 ± 2 MPa). DNSOC and TMSOC increased the transverse strengths by about 30%. DMF on the other hand caused about a 15% a decline in σ_{2u} (These strengths were measured using the short beam test

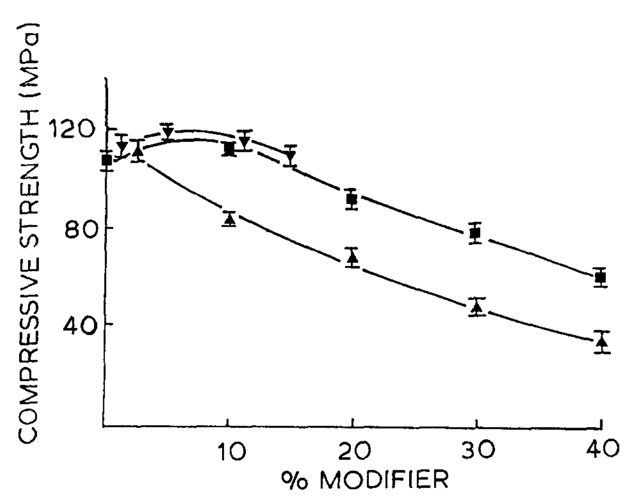


Figure 7 Compressive strengths of fully cured resins plotted against amount of modifier. (Symbols as Fig. 6).

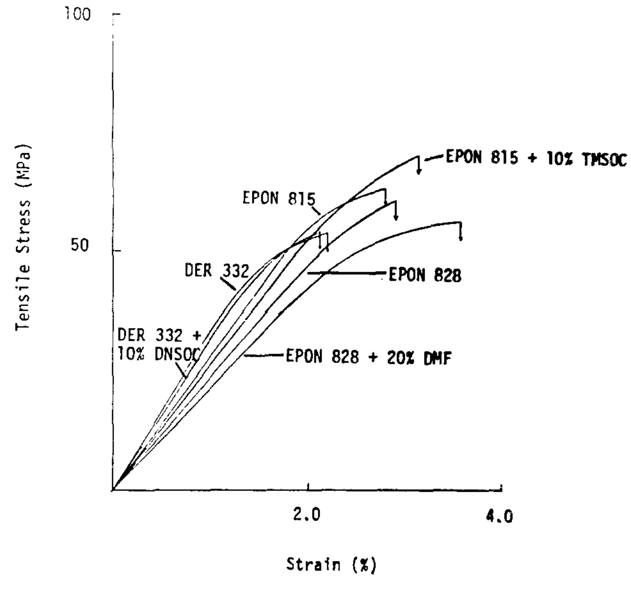


Figure 9 Stress–strain curves for fully cured modified resins.

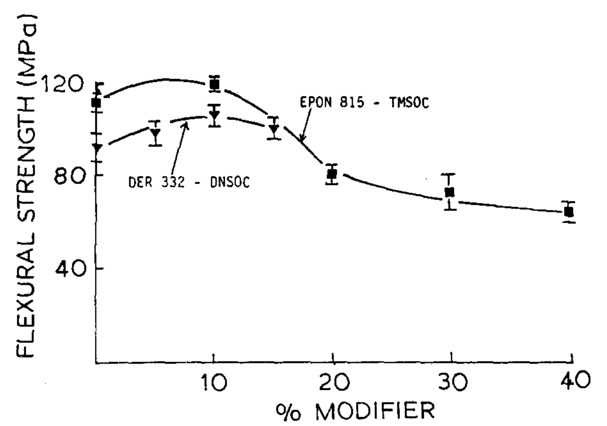


Figure 10 Flexural strengths of fully cured resins plotted against amount of modifier. (▼ DER 332-DNSOC, ■ EPON 815-TMSOC).

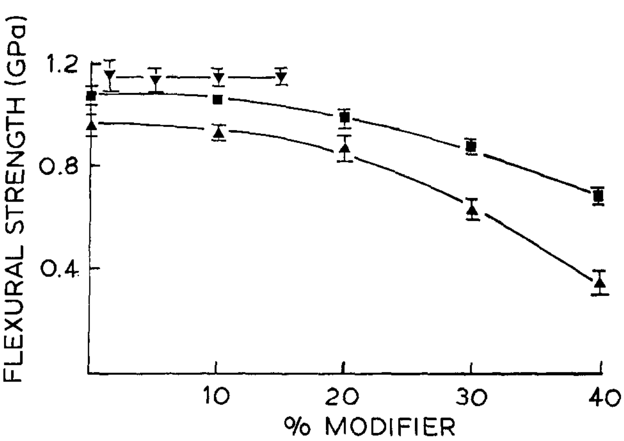


Figure 11 Flexural strengths of carbon fibre pultrusions plotted against amount of modifier in the resin. (Symbols as Fig. 6).

with the fibres aligned in the direction of the centrally applied load.)

SEM pictures of the specimens which underwent transverse tension tests indicated that the fibre–matrix adhesion was strongly affected by the additives. The unmodified resins, Figs 15a and 15b, gave fracture surfaces which showed about 60% of the fibre surface debonded from the resin. The spiros, Figs 15d and 15e gave fracture surfaces with 10% or less of the fibre surface showing, while the DMF and silicone coated fibres gave fracture surfaces with the fibres almost completely debonded, Figs 15c and 15f.

The Izod impact strength of the composites was increased some 50% or more by the use of the expanding monomers, though with TMSOC there appeared to be little benefit in using more than about 20% of the spiro. The DMF caused some loss of toughness, see Fig. 16. The different epoxies gave composites with somewhat different toughnesses, as indicated by the values at the ordinate. Observation of the fracture surfaces indicated that the increase in toughness resulting from the use of the spiros was accompanied by an increase in average fibre pull-out length.

Micrographic observation of the composites before testing indicated that void contents were low, and density measurements gave a value of 1.3 ± 0.1% voids. There were some resin-rich regions, Fig. 17, but these were less evident with the composites made using DNSOC and TMSOC. The fibres were reasonably straight initially, and also after testing.

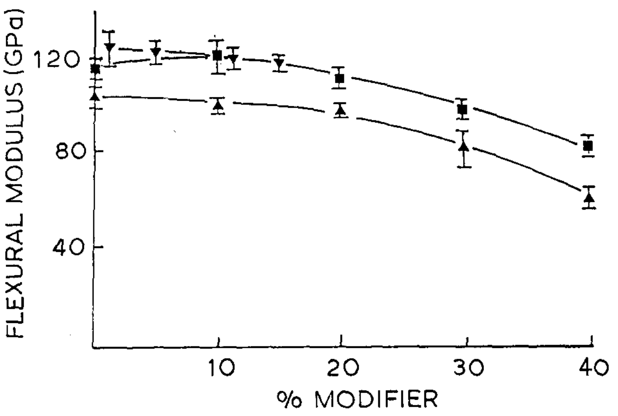


Figure 12 Flexural moduli of carbon fibre composites plotted against amount of modifier in the resin. (Symbols as Fig. 6).

4. Discussion

4.1. Resin properties

Although the strain gauge probe could not be used when curing took place at high temperature, because of the risk of damage to it, the information that it gave at room temperature was compatible with earlier work [4]. This indicated a reduction of shrinkage stress from about 20 MPa to about 7 MPa for epoxy, when $7\frac{1}{2}$% DNSOC was added. This agrees with the result shown in Fig. 3, within the margin of error in the results. TMSOC was not as effective as DNSOC, and the plasticizer, DMF, had surprisingly little stress relieving effect. The shrinkage stresses of the spiro copolymers correlated very well with the densities, Fig. 18.

TABLE II Static properties of carbon fibre pultrusions ($V_f = 0.5$)

Matrix	Tensile strength (GPa)	Young's modulus (GPa)	Compressive strength (GPa)
DER 332	1.11 ± 0.03	108 ± 2	0.83 ± 0.05
DER 332-5% DNSOC	1.09 ± 0.03	108 ± 2	0.80 ± 0.06
DER 332-10% DNSOC	1.06 ± 0.03	109 ± 2	0.86 ± 0.06
DER 332-15% DNSOC	0.98 ± 0.03	109 ± 1	0.84 ± 0.03
EPON 815	1.28 ± 0.04	110 ± 1	0.82 ± 0.04
EPON 815*	1.26 ± 0.03	107 ± 1	0.63 ± 0.05
EPON 815-10% TMSOC	1.27 ± 0.03	107 ± 2	0.84 ± 0.04
EPON 815-20% TMSOC	1.26 ± 0.05	107 ± 2	0.78 ± 0.05
EPON 815-10% DNSOC†	1.06 ± 0.04	112 ± 2	0.85 ± 0.06
EPON 828-20% DMF	1.17 ± 0.06	106 ± 2	0.72 ± 0.04

*Fibres coated with silicon oil.
†Cured with Anchor 1115 at 135° C.

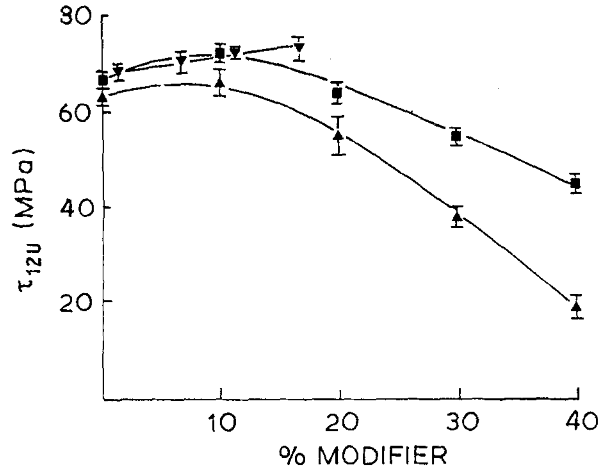
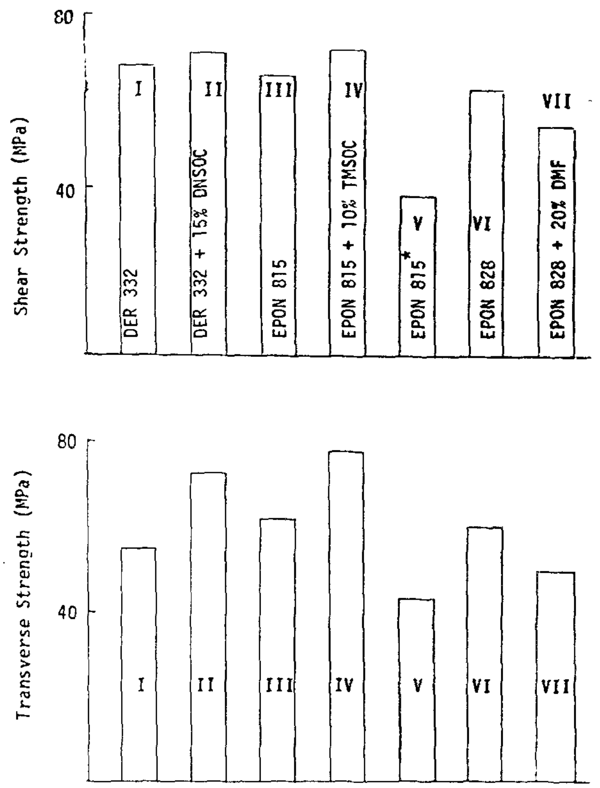


Figure 13 Shear strengths of carbon fibre pultrusion plotted against amount of modifier in the resin. (Symbols as Fig. 6).



*Fibres Coated with Silicone Oil

Figure 14 Shear strengths and transverse tensile strengths of carbon fibre pultrusions made with various resins.

The differences between the measured densities and the rule of mixtures results reflects the steric effects of the additives. DNSOC does not readily fit into the epoxy structure, due to the large size of the norbornene groups. It thus gave a fairly large density deviation, while TMSOC gave a small deviation, and in both cases measured densities were less than theoretical. This effect no doubt enhanced the effect due to expansion on cure, and could account for the greater stress relieving effects of the DNSOC. The plasticizer, DMF, is a relatively small molecule, and could, therefore, fit into the interstices of the structure giving a greater than theoretical density. Because of this, and presumably the relative rigidity of the epoxy, DMF had almost no stress relieving effect.

DNSOC appears to interfere with the elastic deformation of the polymer to a small extent to give the slightly increased Young's modulus shown in Figs 6 (tension) and 8 (compression). Both TMSOC and DMF, on the other hand, had a plasticizing effect (see Fig. 9). This effect was accompanied by a corresponding decline in strength in the case of the DMF. The increase in strength of the spiro-epoxy copolymers was accompanied by some loss of ductility. The flexural strengths appeared to be governed by the compression strength, indicating that these copolymers were brittle. The Young's modulus in compression was about 30 times the compression strength, Fig. 17. A closely similar relation has been observed with polyesters, [5] but it is interesting that the DMF plasticized polymers fit the same line. The flexural

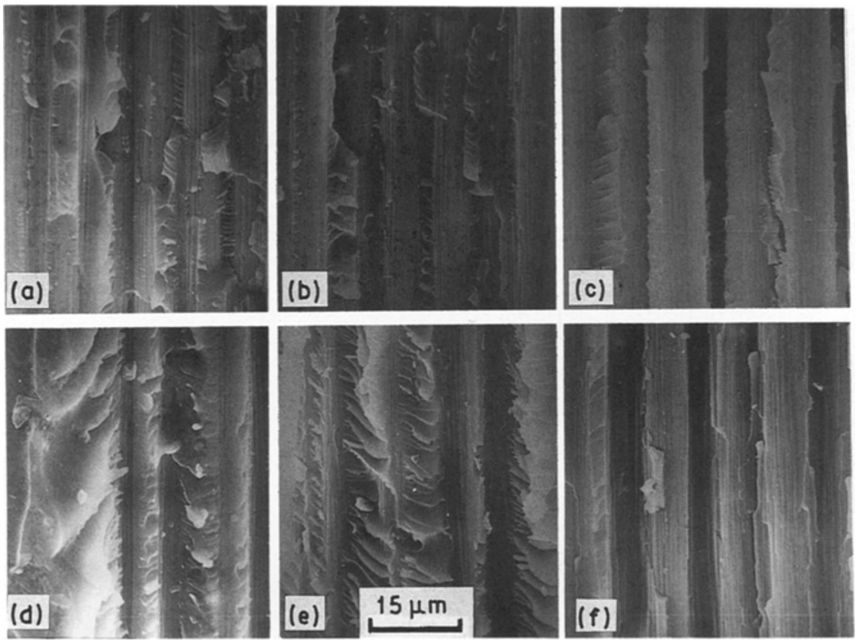


Figure 15 Micrographs (SEM) of fracture surfaces of pultrusions with different resin matrices: (a) DER 332; (b) EPON 815; (c) EPON 828-20% DMF; (d) DER 332-15% DNSOC; (e) EPON 815-10% TMSOC; and (f) EPON 815 with fibres coated with silicone.

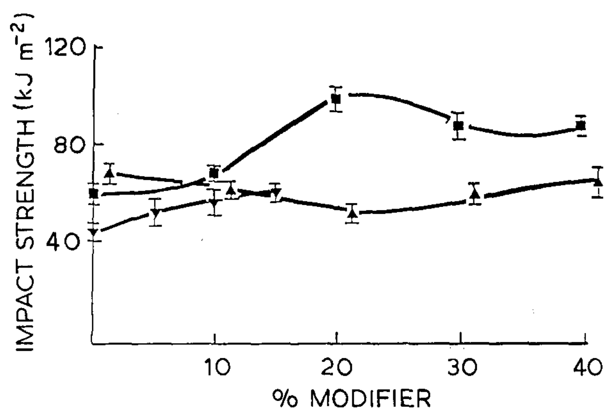


Figure 16 Toughness of carbon fibre pultrusions as measured by Izod test plotted against amount of modifier in the resin. (Symbols as Fig. 6).

strengths of the spiro-epoxy copolymers also fitted the line quite well.

4.2. Composite properties

The tensile properties of composites are controlled by the fibre properties, rather than the matrix, at least when the composites are well made and have reasonably high fibre contents. Thus the loss in strength observed with the 15% DNSOC composites (Table II) was probably due to fibre damage during pultrusion. Since the DNSOC is not very soluble in the resin, this was probably due to abrasion by crystals of the DNSOC. The more soluble TMSOC did not cause any significant change in tensile strength, but may have caused some loss in compressive strength (Table II) at higher concentrations. A similar loss was noted with DMF. These losses were probably due to some extent to the plasticizing effect of these additives (the TMSOC forms a polyoxycarbonate with quite a low T_g, i.e. 123° C).

The effect of the silicone is evident in the compression strength, which is much reduced, in agreement with earlier work that showed that poor fibre–matrix adhesion gives poor composite compressive properties [6, 7]. Some of the compression strength loss resulting from the use of DMF could also have been due to loss of adhesion (see Fig. 15).

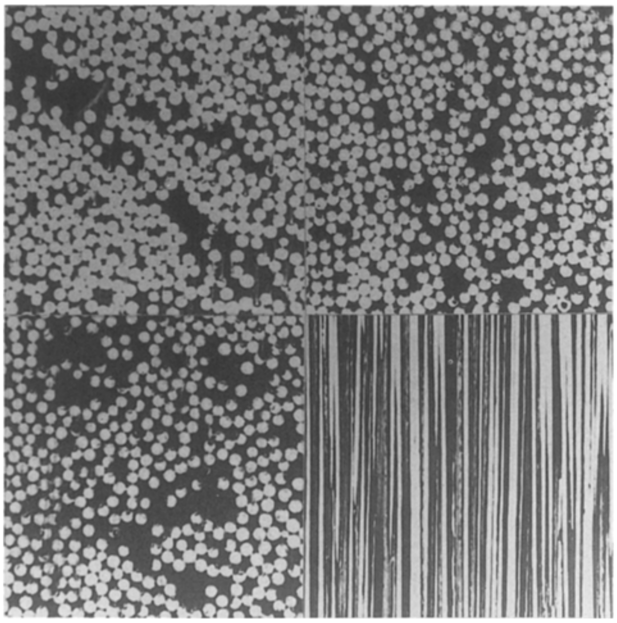


Figure 17 Fibre distributions in pultrusions. Matrices: top left, EPON 815; right, EPON 815-10% TMSOC; bottom left, EPON 828-20% DMF; Bottom right; alignment of fibres in pultrusions.

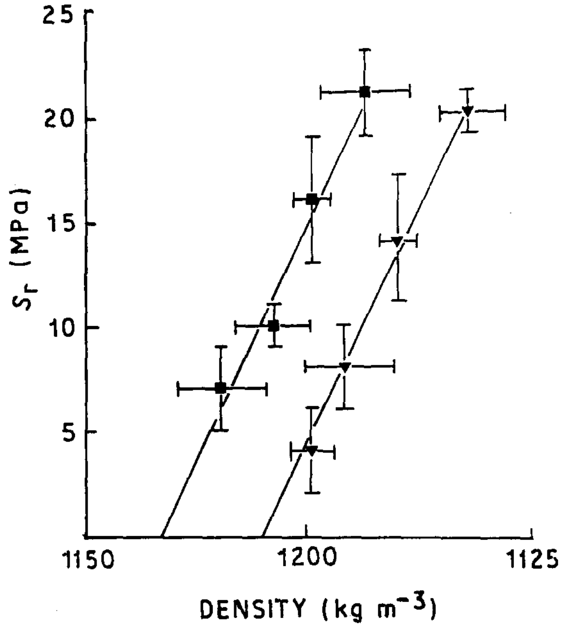


Figure 18 Shrinkage stress plotted against density for controlled shrinkage resins.

The flexural strengths and shear strengths showed similar trends, except that the DNSOC appeared to increase the shear strength without affecting the flexural strength (Figs 11 and 13). The plasticizing effects of DMF, and the TMSOC at higher concentrations were again evident in these properties, and also affected the flexural modulus (Fig. 12). The slight improvement in shear strength with the DNSOC was probably due to improved adhesion (see Fig. 15). Adhesion effects were particularly noticeable in the transverse and shear strength results with DMF and silicone coated fibres, Fig. 14.

The increase in toughness resulting from the use of DNSOC, Fig. 16, was not as great as expected. Two

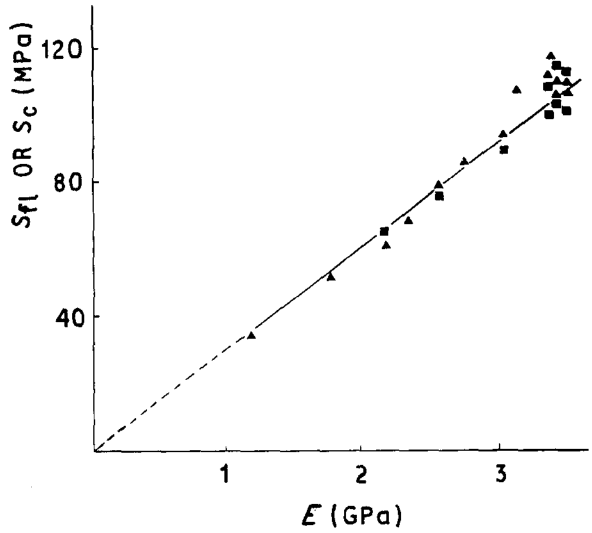


Figure 19 Flexural strength (S_{fl}, squares) and compressive strength (S_c, triangles) plotted against modulus for controlled shrinkage resins.

factors may have contributed to this. The first is the better bonding between fibres and matrix that accompanies the use of DNSOC: in single fibre pull-out studies the fibres usually could not be pulled out of these copolymers at all, unless they were first coated with silicone [8]. The second factor was probably the loss in fibre strength that occurred during the pultrusion process. The theoretical expression for toughness involves the square of the fibre strength [1]. The TMSOC did not appear to cause a loss of fibre strength during pultrusion, and this probably accounts for its greater effect on toughness, at least for additions of up to 20%. The increases in toughness were associated with increases in fibre pulled out lengths at the fracture surfaces. Thus controlling the resin shrinkage was increasing toughness in the way originally envisaged in the patent for this process [9, 10]. In contrast to this, the lack of any effect on toughness of the plasticizer, DMF, is rather surprising. This seems to indicate that in the plasticized matrix the interfacial shears between fibre and matrix are about the same as they were with the unmodified epoxy matrix.

5. Conclusions

The use of expanding monomers to control resin shrinkage increases the toughness of composites without any loss of shear strength, and with only small, and probably avoidable effects on other properties such as tensile strength. DNSOC, although not very soluble in epoxy resins, causes a very large decrease in shrinkage stress, and is probably overall the better of the two spiros tested from the point of view of composite properties generally. The copolymers produced with DNSOC were at least as good as the epoxy homopolymers. The use of the plasticizer, DMF, had little effect on the shrinkage stress and did not improve composite properties.

Acknowledgements

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

References

1. M. R. PIGGOTT, Advances in Fracture Research in Proceedings of the 5th International Conference on Fracture, 1981, Edited by D. Francois. (Pergamon, Oxford, 1981) p. 465.
2. J. T. LIM, M. R. PIGGOTT and W. J. BAILEY, *SAMPE Quart.* **15** (4) (1984) 25.
3. M. S. WOO and M. R. PIGGOTT, *J. Compos. Tech. Res.* **9** (1987) 101.
4. M. R. PIGGOTT and P. S. CHUA, *Ind. Eng. Chem-Product R/D* **26** (1986) 672.
5. M. R. PIGGOTT and B. HARRIS, *J. Mater. Sci.* **15** (1980) 2523.
6. N. L. HANCOX, *J. Mater. Sci.* **10** (1975) 234.
7. M. R. PIGGOTT, *ibid.* **16** (1981) 2837.
8. P. S. CHUA and M. R. PIGGOTT, *Compos. Sci. Technol.* **22** (1985) 245.
9. M. R. PIGGOTT, US Patent 4437725 (1984).
10. M. R. PIGGOTT, European Patent 004 1843 (1987).

Received 21 June
and accepted 8 December 1988