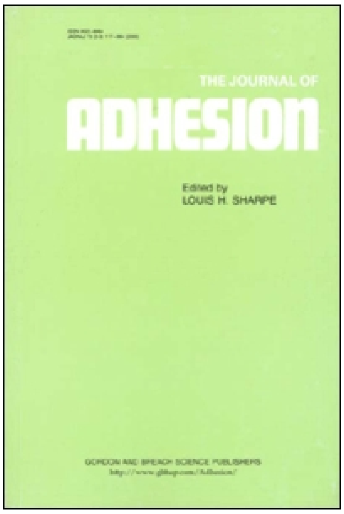

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Thermoplastic Sizing of Carbon Fibres in High Temperature Polyimide Composites*

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Thermoplastic sizing of various carbon fibres has been evaluated as a means of controlling the microcracking resistance, transflexural strength (TFS), and thermo-oxidative stability (TOS) of PMR-15 matrix composites. Four different fibre/thermoplastic size combinations were selected for this study, based on their higher TOS than appropriate controls. Data are presented for the transverse microcrack (TVM) density/inch, and the subsequent delamination of $[0,90]_{4s}$ laminates induced by thermal cycling (-196 to 350°C for 20 cycles). Results for composite TFS, conditioned TFS (after heating in air at 350°C), and TOS (350°C and 316°C) are also reported. One fibre/thermoplastic size combination gave both good microcracking resistance, and significantly improved TOS, in composite when compared with current commercially-available material.

KEY WORDS thermoplastic sizing; carbon fibre; PMR-15; composite; microcracking; thermo-oxidative stability; transflexural strength; delamination resistance; thermal cycling; fibre-matrix interface; transverse microcrack density.

INTRODUCTION

The use of polymer matrix, continuous carbon fibre composites in jet engine manufacture enables significant weight savings to be made over equivalent metal components.[1,2] Current technology primarily utilises epoxy-resin-based systems for lower temperature regimes within the engine, but materials for higher use temperature parts are now being sought. The NASA-developed, thermosetting polyimide PMR-15, with a continuous use temperature of up to 316°C, is one such candidate.[3,4] PMR-15 composites have a major drawback in this application however, namely a poor resistance to microcracking as a result of thermal cycling.[5–9]

Thermal strains develop within PMR-15 composites on cooling from their elevated cure temperature (typically 300–330°C). These strains originate in unidirectional laminates, due to the mismatch between the coefficients of thermal expansion of the fibre and the matrix. In angle-ply laminates, this effect is compounded by the anisotropy of the various plies with respect to thermal expansion. Thus, it can be readily appreciated that (0,90)-type laminates constitute a worst case for microcracking. Thermal cycling within a jet engine, potentially between the continuous use temperature of the PMR-15 composite and freezing conditions, replicates such

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strains and hence promotes microcracking. Due to the characteristic brittleness of all thermosets, this will, at best, compromise component mechanical performance and, at worst, lead to catastrophic failure.

Consequently, various attempts have been made to address the microcracking problem in such composites. Wilson *et al.*[9] examined the effects of cure temperature for (0,90) carbon fibre fabric laminates. Thermal cycling in this case was from −196 to 280°C (for 20 cycles). It was concluded that curing at 280–290°C substantially reduced microcracking, and that mechanical properties were unaffected by the lower temperature cure. The TOS of these materials was studied at only 300°C, however, well below the continuous use temperature of higher cure temperature samples. Furthermore, the glass transition temperature of laminates cured at 280–290°C was lower than for those cured at higher temperatures, again a possible indication of poorer TOS. Pater and Morgan,[10,11] and Sachdeva and Reardon[12] blend-toughened the PMR-15 matrix with thermoplastics to reduce microcracking. Excellent TVM density/inch values were obtained for carbon fibre composites after thermal cycling from −156 to 288°C for 1500 cycles.[10] Such matrices are, of course, fundamentally chemically different from PMR-15. Extensive further investigation will, therefore, need to be done before qualification on aerospace programmes. There is also the question of their ease of processing from high-boiling-point solvents such as n-methyl pyrollidone (NMP).[10]

In this work, a different approach was taken in an attempt to control microcracking in PMR-15 composites, by concentrating on the role of the fibre-matrix interface. Fibre surface finish is well known to affect composite TOS,[13–18] and microcracking too has been shown to be fibre dependent.[16] Here, therefore, novel sizes were used as a means to vary the interface; specifically, reactively-terminated, low molecular weight thermoplastics. The choice of these sizes revolved primarily around a desire to toughen the PMR-15 matrix locally to the fibres, hence improving microcracking resistance. Effects on TFS and TOS were considered secondary, although, with a mechanically stronger, more intimate interface, the opportunity for oxidative attack could be considerably reduced. It should be stressed that there were no changes to the composite cure cycle or resin chemistry introduced in this study, and that thermoplastic sizing only requires sizing technology similar to that currently available. Also, one of the thermoplastics used here is a commercial product, whilst the other two are based on commercial products with the molecular weight and/or end group moeity changed. Thus, no significant new synthetic work was necessary to utilise these materials.

EXPERIMENTAL

Materials

A range of carbon fibres was selected for an initial fibre/thermoplastic size TOS study and, where possible, unsized base fibres were used (Table I). Fibre sizing was carried out with

A: a polyisoimide; M_n 11,000,
B: a polyarylsulphone; M_n 13,000, or
C: an imidised polyarylsulphone; M_n 12,000.

TABLE I
Carbon fibres used in this work

Fibre	Manufacturer	Size	Shape**/Surface+	Diameter (μm)
T650-42	Amoco	Epoxy (UC309)	BI/CR	5.0
T40-R	Amoco	Epoxy (UC304)	RO/CR	6.75
T800	Toray	None	BI/CR	5.0
IM7	Hercules	None	RO/SM	5.0
IM8	Hercules	None	RO/SM	5.0
AS4	Hercules	None	RO/SM	8.0
HTA-7	Akzo	None	RO/CR	7.5
HTA-5001	Akzo	None	RO/CR	7.0
G30-500	Celion	Epoxy (EP03)	RO/CR	6.75

**BI = Bilobal; RO = Round
+CR = Crenelated; SM = Smooth

These were synthesised to have reactive end groups with respect to the proposed PMR-15 crosslinking chemistry[3] (B and C: proprietary to ICI, plc), or were used as supplied (A: from National Starch & Chemical Co.). A single fibre tow (12 K) was pulled through an NMP solution of the appropriate polymer ($\frac{1}{8}$% w/v for A and C; $\frac{1}{16}$% w/v for B). The tow was then dried at 210 ± 5°C. [A drying temperature higher than the boiling point of NMP (202°C) combined with the large surface area of the tow, and a long residence time in the drying tunnel (~30 s) ensured solvent removal]. The line speed of the fibre sizing rig (Figure 1) was ~1.61 m/min. Good quality sizing of individual fibres was achieved under these conditions (Figure 2), rather than thermoplastic deposition around the outside of the tow. The thermoplastic-sized tows had handling qualities similar to their epoxy-sized equivalents, and a quite distinctive sheen.

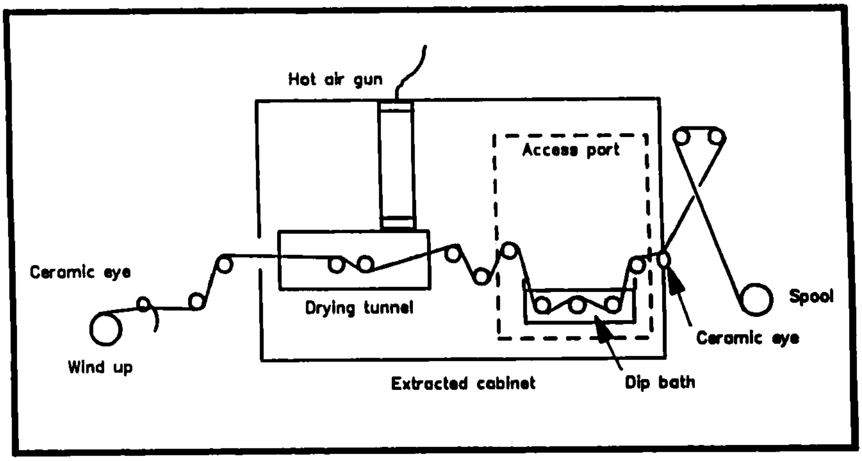


FIGURE 1 Fibre sizing apparatus used in this work.

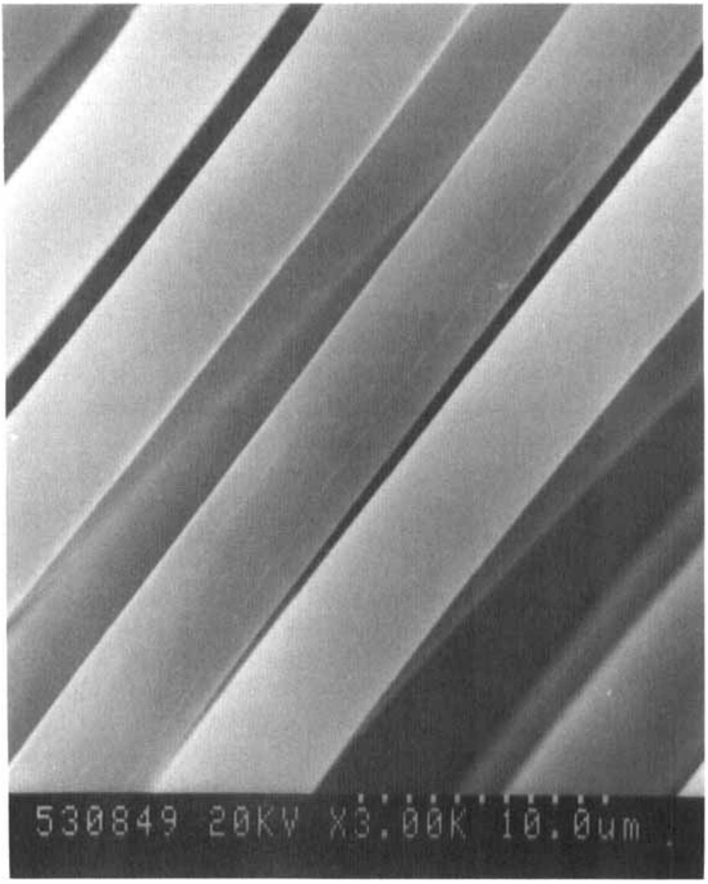
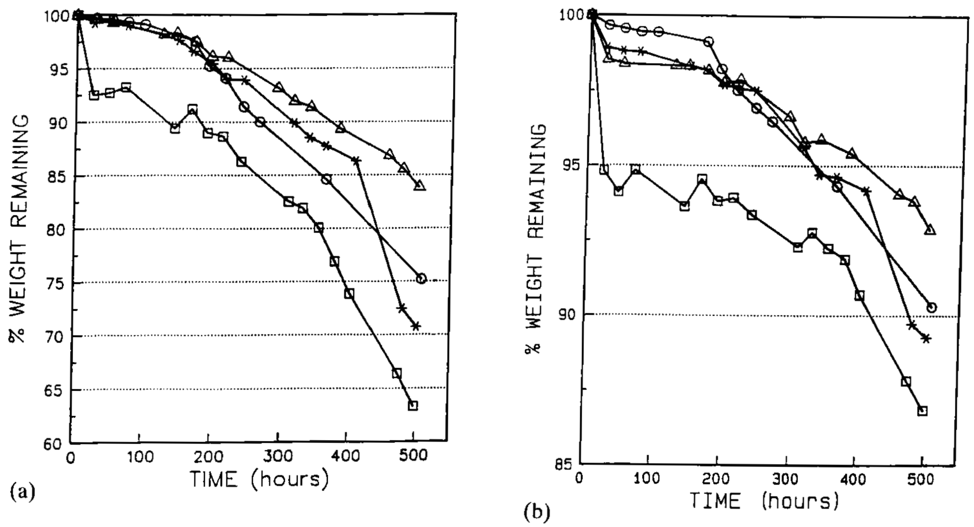


FIGURE 2 Typical thermoplastic sizing quality: IM7(u) fibres/size A.

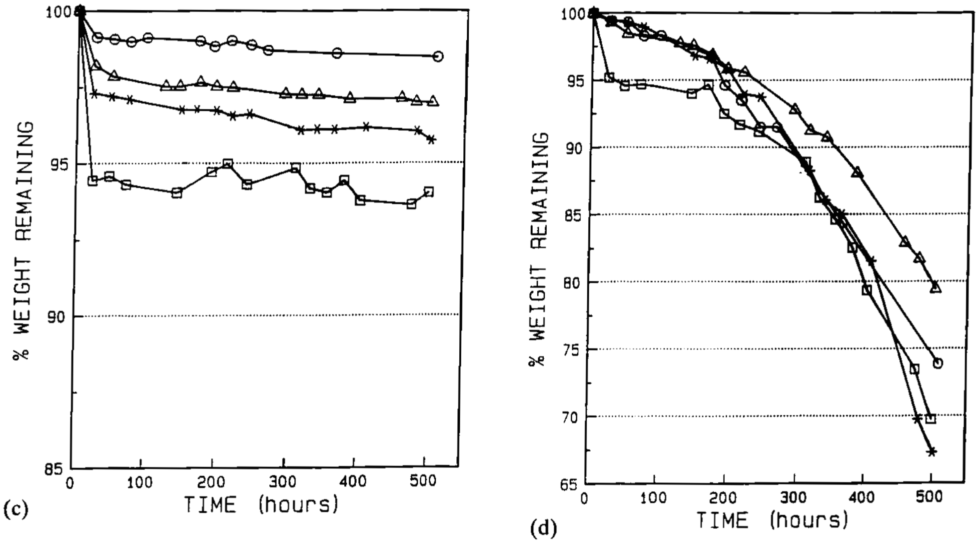
Characterization

The TOS performance of all of the fibres in Table I, sized with each of the thermoplastic sizes, was assessed by periodically measuring weight loss during isothermal ageing at 350°C in an air circulating oven. These experiments were allowed to run for approximately 500 hours (Figure 3). In the case of fibres with an epoxy-compatible size there was an initial weight loss (after ~24 hours) of between 5 and 7.5% [Figures 3(a)–(c) for example], which was ascribed to size burn-off and possible moisture loss in the TOS experiments. Although the drying process used in thermoplastic sizing would probably have removed this moisture, there would have been ample time for the thermoplastic-sized fibres to pick up moisture again from the atmosphere during storage prior to prepregging. That they apparently did not do so, to the same extent as the epoxy-sized fibres, is perhaps indicative of an increased



G30-500 AS RECEIVED IS SIZED WITH EPOXY EP03

T650-42 AS RECEIVED IS SIZED WITH EPOXY UC309



T40-R AS RECEIVED IS SIZED WITH EPOXY UC304

FIGURE 3 TOS data at 350°C for (a) G30-500 fibres, (b) T650-42 fibres, (c) T40-R fibres, and (d) IM7 fibres (* = size A, △ = size B, ○ = size C, and □ = as received).

TABLE II
Fibre/size combinations selected for prepregging

Fibre	Size + +
T650-42	(u)
T650-42	(e)
T650-42	(e)/size A
G30-500	(u)
G30-500	(e)
G30-500	(u)/size A
T800	(u)/size B
IM8	(u)
IM8	(u)/size C

+ + (u) = Unsized
(e) = Epoxy compatible size (as in Table I).

resistance to water contamination. For the G30-500(e) fibre, even if this initial burn-off is discounted, the final (as received) weight loss [of 36.7 − 7.5% *i.e.* 29.2%: see Figure 3(a)] is still greater than that for equivalent size B- and size C-coated fibres (16.2 and 24.8%, respectively). It should also be noted that the thermoplastic-sized fibres are apparently more resistant to water (or other) contamination than even unsized fibres [Figure 3(d)]. The mechanism for water uptake by unsized fibres is perhaps less clear than with epoxy-sized fibres.

As a result of this screening, therefore, four fibre/thermoplastic size combinations were selected for prepregging with PMR-15 resin (Fiberite 966D), along with suitable controls (Table II). Note that G30-500(u)/size A rather than G30-500 (e)/size A was chosen, as this allowed an examination of the effect of retaining the epoxy compatible size prior to thermoplastic sizing [G30-500(u)/size A *vs* T650-42(e)/size A]. Each prepreg was fabricated at 145 g/m^2 fibre areal weight, and 40% resin content. There was a noticeable increase in the wettability of the thermoplastic-sized fibres during prepregging, compared with unsized or epoxy-sized equivalent fibres.

These prepregs were than laid up as $[0,90]_{4s}$ and $[0]_{16}$ laminates (each 15 × 10 cm) for TVM and TFS testing, respectively. The imidization, cure and postcure cycles were as shown in Figure 4. Note that the use of 1000 psi (6.9 MPa) consolidation pressure during the cure cycle is only necessary because of the compression moulding technique used.[19] Such pressure is required to ensure good contact of the two mould halves with the laminate. Autoclave cure of these systems at 200 psi (1.4 MPa) consolidation pressure is obviously viable, as the matrix resin is standard PMR-15. All laminates were examined with ultrasonic C-scan, and were found to be void-free.

Thermal cycling from − 196 to 350°C (20 cycles) was performed on 2.5 cm square samples, cut from the $[0,90]_{4s}$ laminates with their edges parallel to the fibre directions. Such cycling is comparable with that used in Reference 9. The TVM density/inch was determined by sectioning these along the 45° direction, this face being polished before examination by scanning electron microscopy. Delamination was sometimes detected in addition to microcracking, and was quantified as a percentage of the total laminate interply zone length.

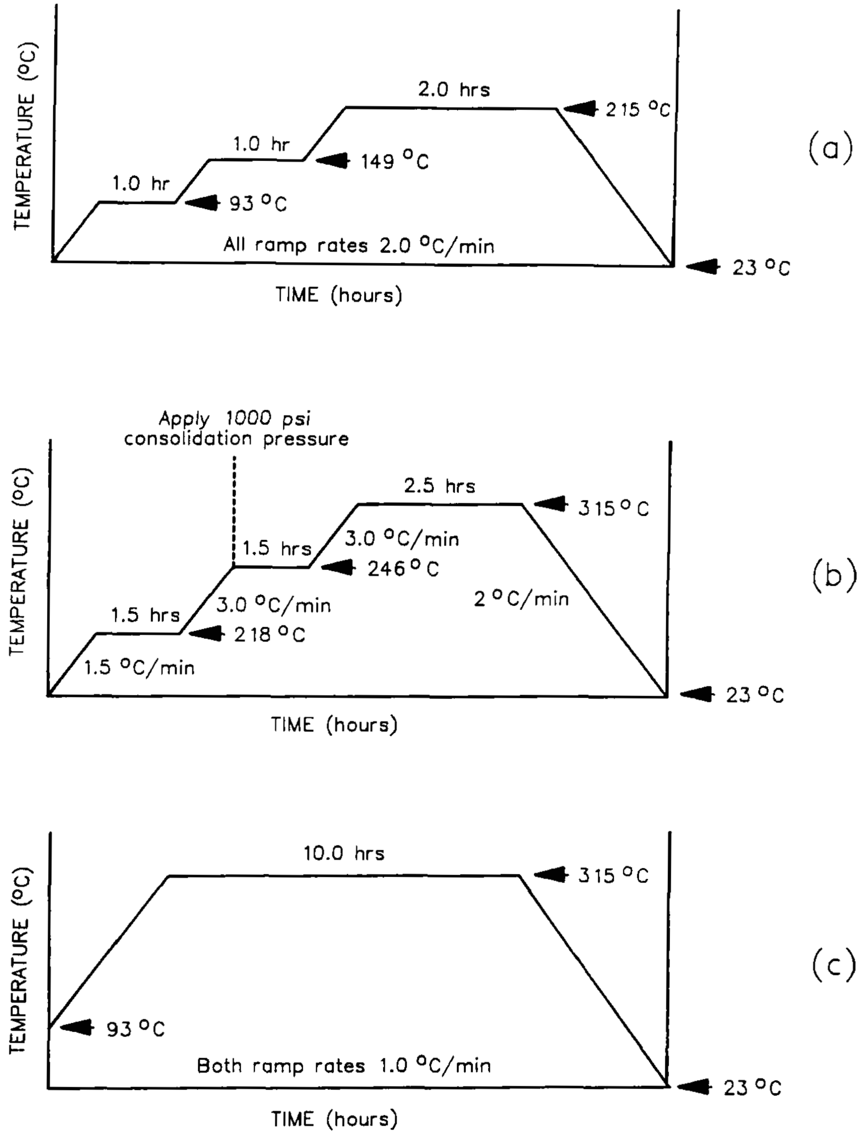


FIGURE 4 Conditions used for (a) imidization, (b) cure and (c) postcure of the PMR-15 laminates.

TFS testing of the $[0]_{16}$ laminates was carried out to ASTM Standard D-790, following a three-line bending test method, modified for high modulus composites. Conditioned TFS samples were also tested, after heating at 350°C in an air circulating oven for 150, 310 and 387 hours.

Finally, composite TOS measurements were made as for the initial fibre/thermoplastic size combinations, at both 350 and 316°C.

RESULTS AND DISCUSSION

Figures 5 and 6 show the TVM density/inch and delamination data, respectively, from the thermal cycling experiments for the $[0,90]_{4s}$ laminates of Table II. In Figure 5 it can be seen that the interface undoubtedly plays a key role in the microcracking mechanism. For the same fibre type (G30-500, T650-42 or IM8), there is a pronounced effect due to sizing on the TVM density/inch. In the case of G30-500 fibre, the epoxy-compatible size is most favourable, whilst for T650-42 fibre the opposite is true, with the thermoplastic-sized and unsized variants performing equally well. For T650-42 fibre, size A appears to reduce microcracking substantially compared with the epoxy compatible size, whereas, with G30-500, size A gives the worst result. This apparent contradiction may be explained in that G30-500 was used unsized, whereas T650-42 had an epoxy-compatible size to begin with. Size A would appear, therefore, to be more effective on fibres presized with an epoxy-compatible size. The very good microcracking resistance of PMR-15 composite with unsized T650-42 fibres should also be noted. The practical difficulties in handling unsized fibre, however, such as in fabric weaving, may limit the application of this result. Size C on unsized IM8 fibre also performs badly in this test, perhaps indicating a need for presizing with an appropriate epoxy-compatible size before thermoplastic sizing. Size B, however, on T800 unsized fibre, appears to give good microcracking resistance in composite, although this could not, unfortunately, be compared with a control due to a shortage of this fibre. Such data should, therefore, be considered carefully because, as in the case of T650-42(u) fibre, it may be that T800(u) fibre reduces microcracking independently of the type of size used. From the results of Figure 5, however, it appears that T650-42(u), T650-42(e), T650-42(e)/size A, and T800(u)/size B are worthy of further consideration as fibre/size combinations. [G30-500(e) is no longer commercially available]. The properties of the composites with thermoplastic-sized fibres are best compared with those of the T650-42(e) based laminate, as the T650 family is currently preferred commercially in these materials. Also, it should be mentioned that the G30-500(u)/size A, T650-42(e) and IM8(u) laminates each had a TVM density/inch of ~8 before thermal cycling, the others all being microcrack free after postcure.

In Figure 6 similar trends to the above are seen with the delamination data for these composites. Of particular note are the results for the T650-42(u), T650-42(e)/size A and T800(u)/size B fibre/size combinations. All of these give significantly improved delamination resistance in composite compared with T650-42(e) fibres, and the T800(u)/size B fibre/thermoplastic size combination is quite outstanding in this respect. Figure 7 shows micrographs of the thermally-cycled PMR-15 composites with T800(u)/size B and T650-42(e) fibres. The latter [Figure 7(a)], has extensive microcracking, delamination, and other voidage after the extremely rigorous thermal cycling used. The T800(u)/size B based PMR-15 composite, however, has only minor microcracking by comparison.

Figure 8 shows the results from TFS testing of the $[0]_{16}$ laminates from Table II. For each fibre type there is some improvement in unconditioned TFS performance with thermoplastic sizing over the other sizes considered. [For T800(u)/size B fibres

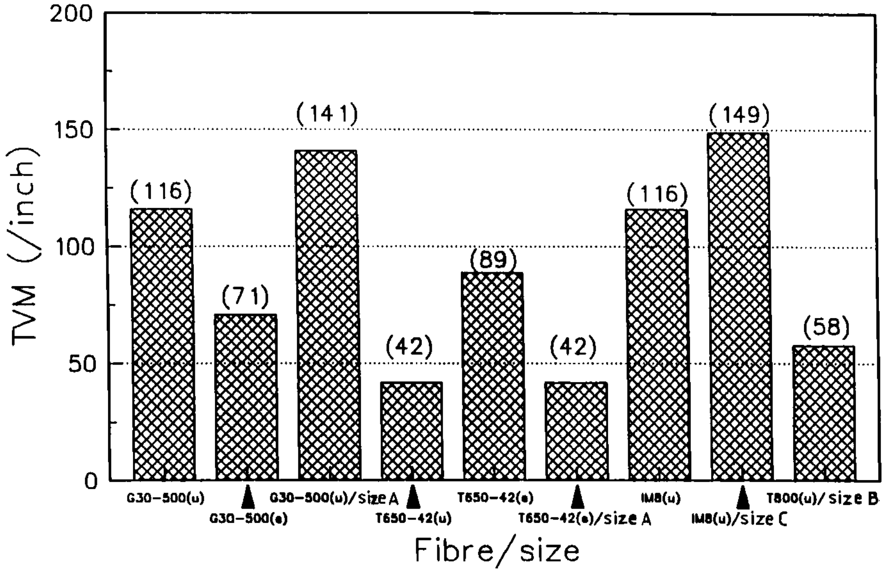


FIGURE 5 TVM density/inch of $[0,90]_{4s}$ PMR-15 laminates with various fibre/size combinations, after thermal cycling (− 196 to 350°C for 20 cycles).

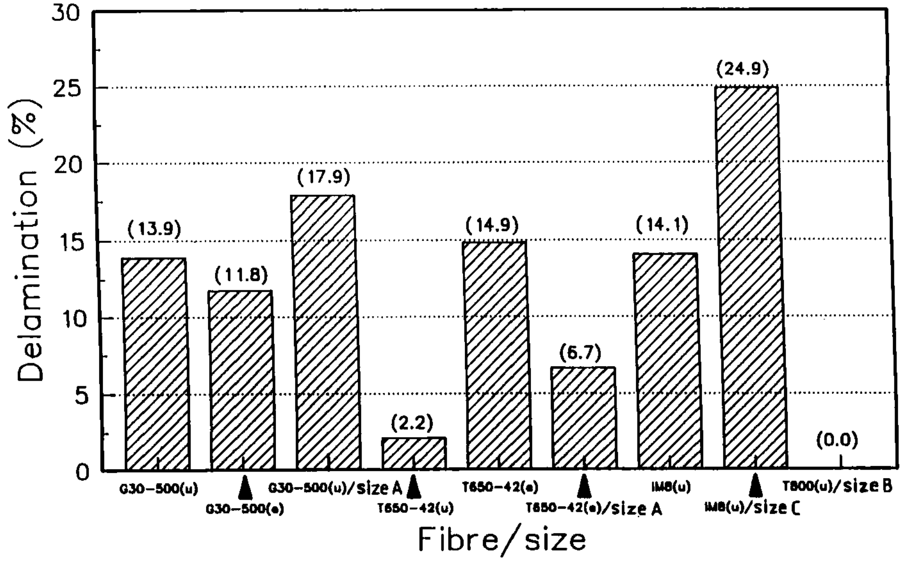
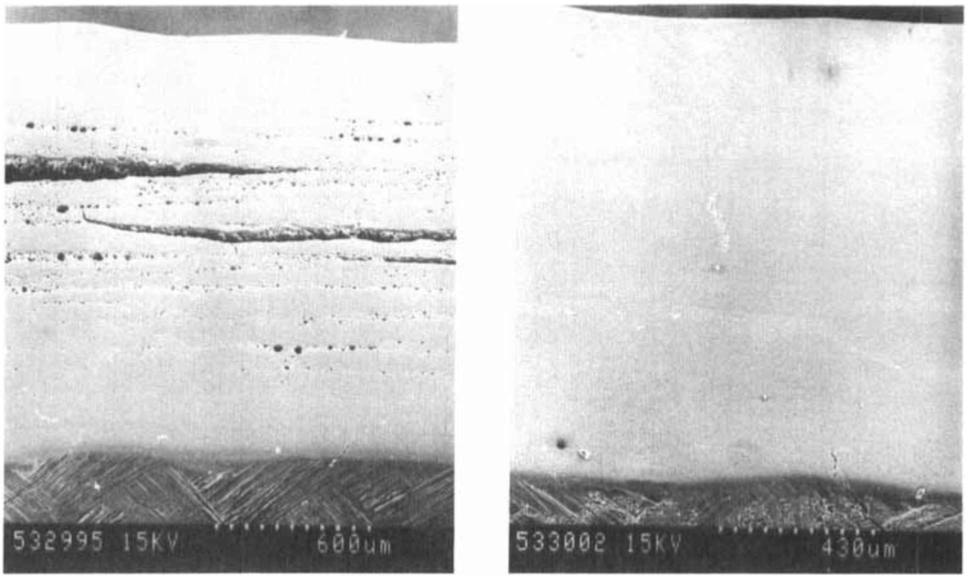


FIGURE 6 Delamination as a percentage of the total laminate interply zone length, for $[0,90]_{4s}$ PMR-15 laminates with various fibre/size combinations (thermal cycling was as for Figure 5).



(a) (b)

FIGURE 7 Damage induced in $[0,90]_{4s}$ PMR-15 laminates by thermal cycling as for Figure 5: (a) T650-42(e) fibres, and (b) T800(u)/size B fibres.

again no control could be made]. The two favoured thermoplastic-sized fibres from the thermal cycling experiments [T650-42(e)/size A and T800(u)/size B], both have acceptable unconditioned TFS values in composite (94.0 and 67.6 MPa, respectively). There is little to choose, however, between the conditioned TFS performances of thermoplastic and equivalent conventionally-sized fibres. The only significant data is the poorer performance of G30-500(u)/size A PMR-15 composite, compared with the G30-500(u) and G30-500(e) based materials. The composites using T650-42(e)/size A and T800(u)/size B fibres again show acceptable results in this test.

Finally, Figure 9 illustrates the TOS performance at 350°C of the various fibre/thermoplastic size combinations in composite, compared with that for T650-42(e) fibres (for the reasons described above). Once more, the two favoured thermoplastic-sized fibres outperform T650-42(e). Indeed, T800(u)/size B has the best TOS performance in composite of all the fibre/size combinations studied (Table III), losing only 8.9% w/w after 500 hours at 350°C. Also, there is evidence here that this is due to the thermoplastic size rather than to the unsized fibre, as the TOS of T800(u)/size B fibre exceeds that of the T800(u) fibre quite considerably (10.0 *vs* 17.6% weight loss after 500 hours at 350°C, respectively). Furthermore, it should be noted that T800(u) fibre has a poorer TOS than T650-42(e) fibre (17.6 *vs* 13.2% weight loss after 500 hours at 350°C); thus, with appropriate thermoplastic sizing in composite, the former has produced a markedly-better TOS than the latter.

Table III also shows equivalent results at 316°C for composite TOS, as well as other appropriate fibre TOS data. In addition, comparisons can be made from Table

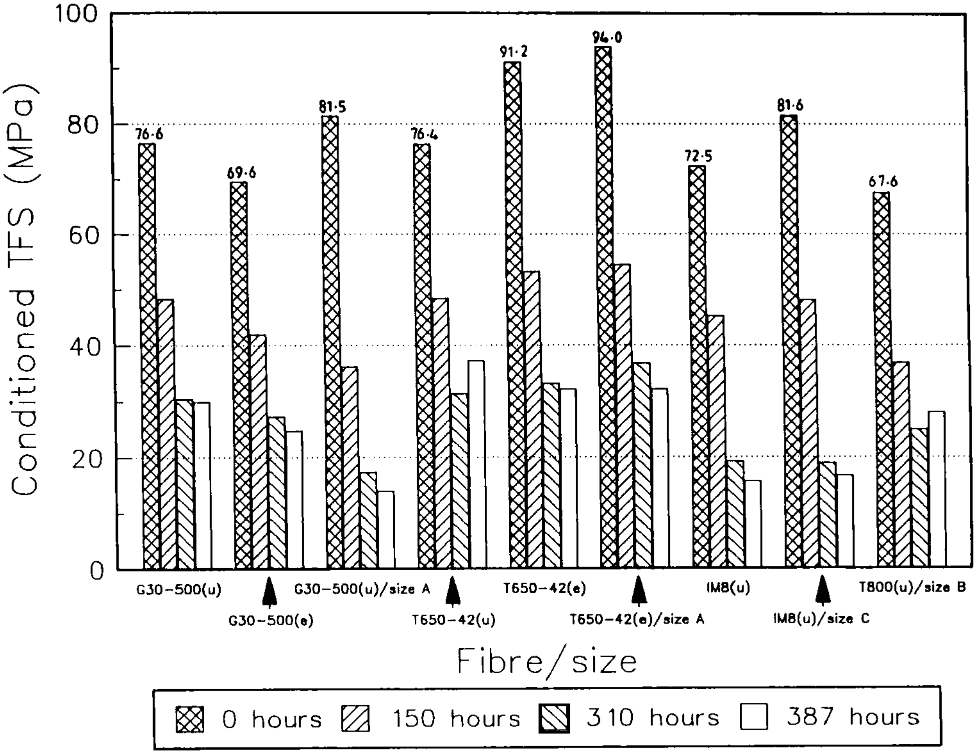


FIGURE 8 TFS of $[0]_{16}$ PMR-15 laminates with various fibre/size combinations (conditioned at 350°C; room temperature testing).

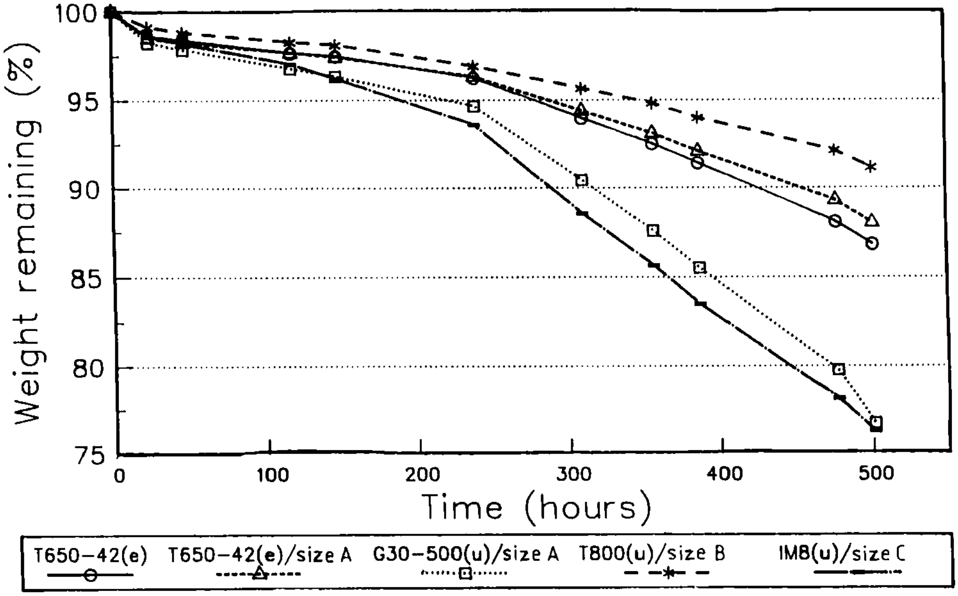


FIGURE 9 TOS at 350°C of $[0]_{16}$ PMR-15 laminates with various fibre/size combinations.

TABLE III
Composite and appropriate fibre weight loss after 500 hours at 350 and 316°C

Fibre in PMR-15 composite	Fibre weight loss after 500 hours (%)	Composite weight loss after 500 hours (%)	
	350°C	350°C	316°C
T650-42(u)*	—	11.7	2.5
T650-42(e)	13.2	13.2	2.8
T650-42(e)/size A	10.8	12.0	2.7
G30-500(u)*	—	13.8	3.0
G30-500(e)	36.7	15.0	3.4
G30-500(u)/size A*	—	23.3	4.9
T800(u)/size B	10.0	8.9	2.0
IM8(u)	13.1	22.9	3.1
IM8(u)/size C	13.8	23.7	3.6

*Not tested for TOS in initial fibre study; chosen for prepregging for comparative purposes.

III regarding TOS performance due to different sizes on the same fibre type. With the exception of G30-500(u)/size A, it can be seen that the thermoplastic sizing used here gives comparable (IM8 fibres), or slightly improved, composite TOS performance (T650-42 fibres). Obviously no such comparison can be made for the T800(u)/size B based material.

CONCLUSIONS

The microcracking and delamination resistance of PMR-15 carbon fibre composites during thermal cycling have been shown to be strongly dependent on the fibre-matrix interface. With different sizes on the same fibre type, pronounced changes in these properties have been observed and, in some cases, improvements made, through choice of size. For T650-42 fibre the unsized variant showed a lower TVM density/inch than its epoxy-sized equivalent, although it is unlikely that T650-42(u) would be sufficiently damage tolerant in the fabric weaving process for practical applications. Additional thermoplastic sizing on T650-42(e) fibre with size A decreased the TVM density/inch to a level equivalent to the T650-42(u) fibre, however. T800(u) fibre sized with thermoplastic size B produced low microcrack densities, and zero percent delamination, after thermal cycling in composite. This is much improved on the performance of the current commercial fibre/size combination of choice, namely T650-42(e). As there was no control to this experiment it cannot be concluded whether, as with T650-42 fibre, these improvements were due to the change to unsized fibres or to the thermoplastic size used. In addition, thermoplastic sizing has been shown to give some improvement in unconditioned composite TFS for the fibres examined here and, in all but one case, had no adverse effect on conditioned TFS (after heating in air at 350°C). Finally, increases in both fibre and thence composite TOS can be achieved through thermoplastic sizing. Epoxy-sized fibres show an initial burn-off of size and moisture at 350°C, which equivalent thermoplastic-sized fibres seem less susceptible to. Even allowing for this initial burn-off it appears that thermoplastic sizing improves the thermal stability of the fibres concerned [see Figure 3(a)]. Size B proved the most thermally stable here, and this was translated to the composite samples (Figure 9). When unsized fibres were sized using these thermoplastics there was a noticeable increase in sheen, damage tolerance and also in wettability of the fibres during prepregging with PMR-15 resin.

Acknowledgements

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