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Silicon carbide fibre-reinforced resin matrix composites

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Resin matrix composites reinforced with silicon carbide yarn and silicon carbide monofilament were fabricated and evaluated. Both composite systems exhibited excellent mechanical properties. Composite thermal expansion behaviour, fibre electrical resistance, and fibre thermal oxidation resistance are also reported. Advantages with respect to carbon fibre-reinforced resins are discussed.

1. Introduction

Graphite fibre-reinforced resin matrix composites offer many structural advantages due to their high strength and elastic stiffness combined with extremely low density. No other currently available fibre can achieve the high levels of composite performance possible with graphite. Despite this overall structural superiority, however, there are several specific deficiencies which suggest that other fibre reinforcements may be of interest. These shortcomings include the following:

(a) Graphite fibre-reinforced resins do not have very high compression strengths.

(b) Graphite fibre is readily oxidized at elevated temperatures. Although this may not be a problem for current low-temperature resin matrix composites, it can be a major barrier to the development of resin matrix composites for prolonged use at high temperatures.

(c) Graphite fibres and their composites are electrically conductive. Although in some cases this may be an advantage, it is often a disadvantage. Although not a serious hazard, fragments released from incinerated and damaged composites can cause shorting of electrical systems [1]. Also, the difference in electronegativity of graphite-reinforced resin composites and metals can cause preferential chemical attack of attached metal in suitable environment [2].

(d) Graphite fibre-reinforced resins exhibit unique surface wear characteristics. In many cases, particularly for the case of high elastic modulus fibre reinforcement, both the coefficient of friction and wear rate, against a metal counterface, can be quite low. In the case of the lower elastic modulus graphite, however, against some metals the wear rate and frictional coefficient can be very high [3].

The use of silicon carbide fibres to reinforce resins may provide composites which can overcome the above inadequacies. The investigation described herein will demonstrate that two distinctly different forms of continuous silicon carbide fibre can be used to create epoxy matrix composites with excellent properties.

2. Materials and composite fabrication

2.1. SiC yarn–PR-286 resin

The silicon carbide yarn utilized in the research programme was purchased from the Nippon Carbon Co., Japan. The manufacturing process involves synthesis from an organometallic precursor as described by Yajima and co-workers [4, 5]. The fibre was supplied as continuous tows approximately 500 m in length. Fibre count was 250 fibres per tow. Average fibre diameter was 10 μm, although considerable variation in fibre diameter was evident, and the fibre density was 2.7 gm cm^{-3}. The as-received fibre included an organic binder to minimize fraying during handling. This binder was removed by passing the yarn through the flame of a bunsen burner prior to impregnation with resin. PR-286 resin obtained from 3M Co. was selected as the matrix. The resin was diluted with methyl-ethyl ketone resulting in a solution containing 50 wt% resin. Composite preimpregnated tape material was fabricated from these constituents using standard wet-winding procedures and the

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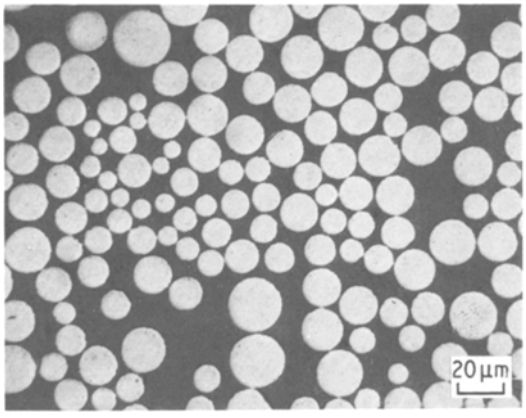

Figure 1 Microstructure of silicon-carbide yarn reinforced PR-286 resin.

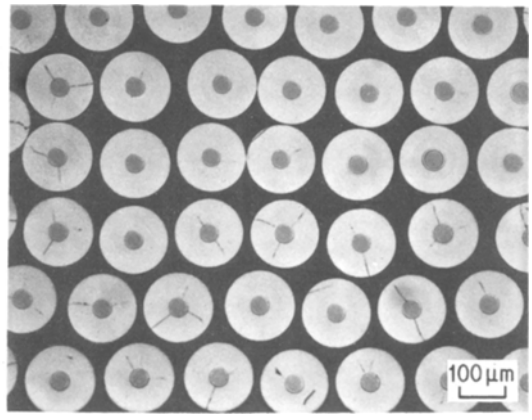

Figure 2 Microstructure of silicon-carbide monofilament reinforced 5506 resin.

resultant tapes were then heated for 2 h at 80° C in a vacuum oven to drive off the solvent.

Unidirectional composites were fabricated by hot-pressing laminates for 1 h at 177° C under 0.69 MPa pressure in a closed steel die. The hot-pressed laminates were then post-cured for 4 h at 177° C in an air circulating oven. The fibre volume-fraction obtained using this procedure was 0.48. A typical composite cross-section is shown in Fig. 1. The composite density was 1.96 gm cm^{-3}.

2.2. SiC monofilament–5506 resin

The silicon carbide monifilament used was manufactured at AVCO Specialty Materials Division by using the technique of chemical vapour deposition of silicon carbide onto a carbon core. The fibre diameter was approximately 140 μm and the fibre density was 3.1 gm cm^{-3}. The fibre was surface-treated by the manufacturer to provide better resin-to-fibre bonding and was obtained in a pre-impregnated tape 76 mm in width incorporating the monofilament with 5506 resin. The as-received tape was pretreated for 1 h at 70° C in a vacuum oven, prior to composite fabrication, since this procedure decreased porosity in the finished composite panels.

Unidirectional composites were fabricated by hot-pressing laminates in closed steel dies in both vacuum bag and air atmosphere using a cure schedule recommended by the manufacturer. Since equivalent flexural properties were obtained using both procedures, pressing in an air atmosphere was adopted as the standard procedure because of its relative simplicity. The hot-pressing procedure entailed curing for 1.5 h at 177° C under 0.69 MPa pressure in closed steel dies. The hot-pressed laminates were then post-cured for 4 h at 190° C. The fibre volume-fraction obtained using this procedure was 0.57. A typical composite cross-section is shown in Fig. 2. The composite density was 2.35 gm cm^{-3}.

3. Composite properties

3.1. Tension and compression strengths

Parallel-sided specimens of dimensions 1.27 mm × 6.35 mm × t mm were cut from the composite panels for tension and compression testing. For the tensile specimens, fibreglass doublers were bonded to the specimens providing a gauge-length of 25.4 mm. For the compression specimens, tapered steel doublers of the appropriate length were used, conforming with ASTM standard D3410 [6]. The compression specimens were fabricated with sufficient thickness to yield a true

TABLE I Room-temperature mechanical properties of SiC-yarn reinforced PR-286 resin

Test	Fibre orientation	V_f	Strength (MPa)	Modulus (GPa)	Failure strain (%)
Tension	Axial	0.48	875	106	0.84
Tension	Transverse	0.48	45.5	17.4	0.29
Compression	Axial	0.50	1200	117	1.14
Compression	Transverse	0.48	107	17.6	1.05

TABLE II Room-temperature mechanical properties of SiC-monofilament reinforced 5506 resin

Test	Fibre orientation	V_f	Strength (MPa)	Modulus (GPa)	Failure strain (%)	Poisson ratio
Tension	Axial	0.57	1410	222	0.65	0.19
Tension	Transverse	0.57	61.3	22.2	0.33	0.015
Compression	Axial	0.59	1990	253	0.85	–
Compression	Transverse	0.57	161	20.6	0.84	–

compressive failure rather than a buckling failure, as predicted from the Euler equation. Both the tension and compression tests were performed using a cross-head speed of 1.27 mm min^{-1}.

The tensile and compressive properties determined at room temperature are listed in Tables I and II for the SiC-yarn-reinforced PR-286 and the SiC-monofilament reinforced 5506, respectively. Even after normalizing to the same fibre volume-fraction, the superior strength and modulus of the SiC monofilament result in higher axial composite tensile strength and modulus. However, the failure strains are greater for the SiC-yarn reinforced resin. Typical tensile stress–strain curves are shown in Fig. 3. Greater differences are observed in axial compressive properties, particularly compressive strength. The large-diameter SiC monofilament resists fibre failure by buckling and allows the composite to achieve a very high compression strength, typically 1990 MPa. The average fibre diameter of the SiC yarn is approximately 7% of that of the monofilament and the yarn elastic modulus is only 50% of that of the monofilament so that yarn-reinforced composites are much more susceptible to microstructural fibre buckling failure in compression. The compression strength of the yarn reinforced composites was 1200 MPa. Typical compression stress–strain curves are shown in Fig. 4.

The SiC-monofilament reinforced composites also exhibited significantly greater transverse tensile and compression strengths, compared with those of the SiC-yarn reinforced composites. This difference is probably related to the fact that the monofilament was surface-treated to enhance bonding to the resin while no such surface treat-

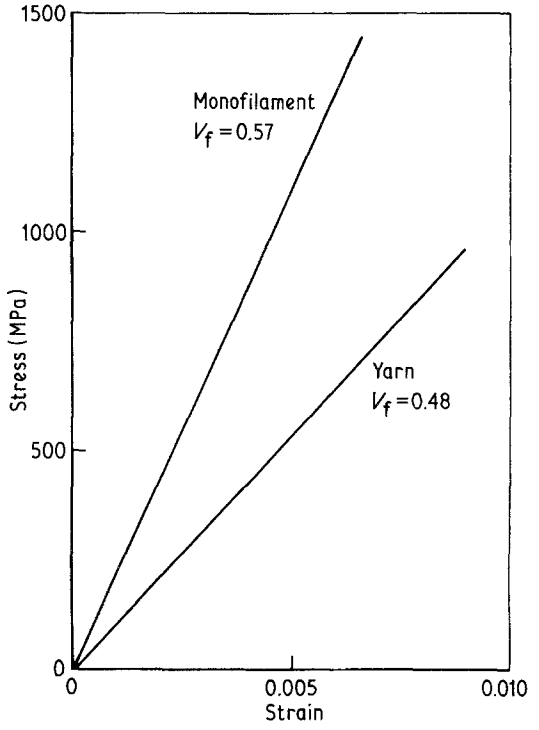

Figure 3 Axial composite tension stress–strain behaviour.

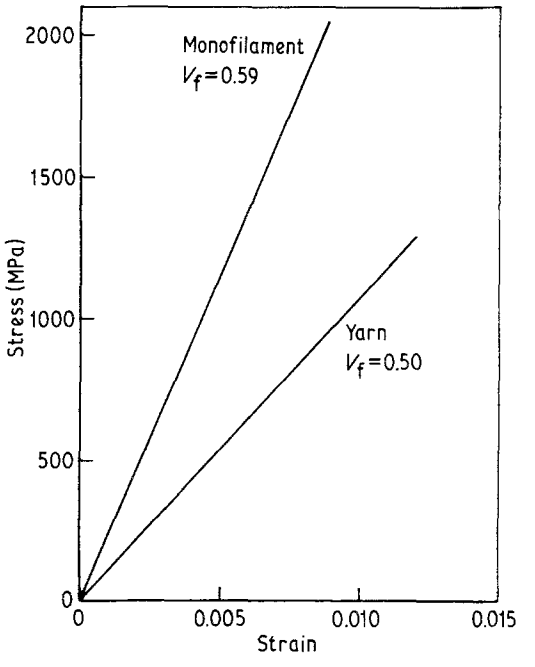

Figure 4 Axial composite compression stress–strain behaviour.

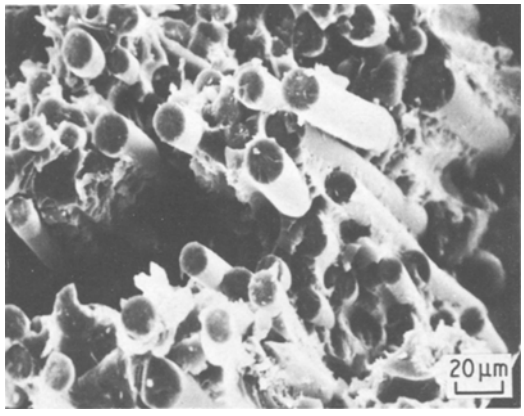

Figure 5 Axial tensile fracture surface of silicon-carbide yarn reinforced resin.

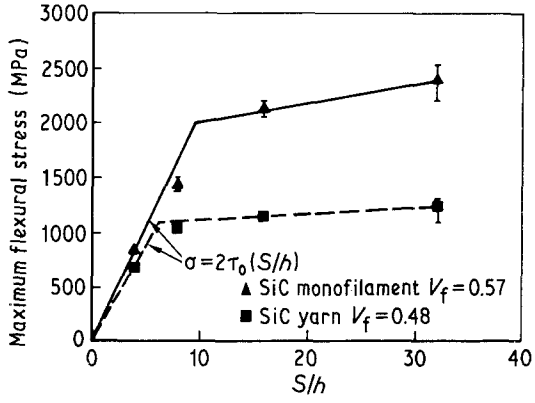

Figure 7 Composite maximum flexural stress as a function of test span-to-depth ratio.

ment was applied to the yarn and no attempt was made to select a more compatible resin. Greater transverse tensile failure strain was also achieved for the monofilament-reinforced composites.

Scanning electron microscope (SEM) observations of both axial and transverse composite fracture surfaces also indicated that better resin–fibre bonding was achieved with the SiC monofilament. As shown in Fig. 5, the axial tensile fracture surface of SiC-yarn reinforced composites exhibits extensive fibre pull-out. In comparison, a monofilament-reinforced composite fracture surface, as shown in Fig. 6, is relatively flat and exhibits only minor pull-out. When one considers the large differences in fibre strength and diameter between these two fibres it is clear that the bonding of the monofilament to the matrix must be much better than that of the yarn to the matrix to cause this large difference in fracture appearance. These results are due mainly to the fact that no effort was made to optimize bonding in the yarn-reinforced composite. A yarn surface treatment or better resin selection could probably improve transverse properties significantly.

3.2. Flexural properties

The composite flexural properties were determined by testing unidirectional composite beams 6.35 mm in width using the three-point bending technique. Testing was performed at a constant cross-head speed of 1.27 mm min^{-1}. The results of the three-point bend tests are plotted in the form of flexural and shear interaction diagrams [7] in Figs 7 and 8, respectively. Figs 7 and 8 demonstrate that the ratio of outer fibre tensile stress to mid-plane shear stress is a function of the test span-to-height ratio, S/h.

Simple equations exist for the prediction of the nominal levels of maximum shear stress and flexural stress generated during the three-point bend testing of a beam of rectangular cross-section.

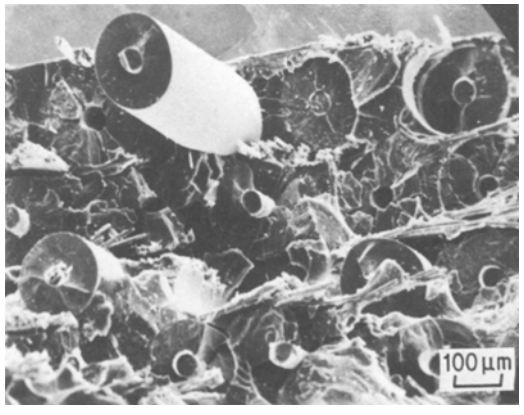

Figure 6 Axial tensile fracture surface of silicon-carbide monofilament reinforced resin.

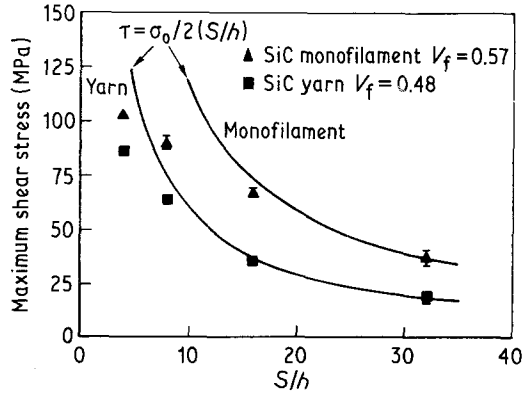

Figure 8 Composite maximum shear stress as a function of test span-to-height depth ratio.

TABLE III Axial composite three-point bend properties determined at room temperature

Fibre	V_f	S/h	Flexural strength (MPa)	Flexural modulus (GPa)	Interlaminar shear strength (MPa)
SiC yarn	0.50	4	–	–	87.2
SiC yarn	0.48	32	1240	99.8	–
SiC monofilament	0.57	4	–	–	103
SiC monofilament	0.57	32	2410	230	–

For a given load P, bending span length, S, specimen depth, h, and width, b, the maximum shear stress occurring at the neutral axis, τ_{max}, can be given by

$$\tau_{max} = \tfrac{3}{4}P/bh. \quad (1)$$

The maximum flexural stress, σ_{max}, occurring at the same time is

$$\sigma_{max} = \tfrac{3}{2}(PS/bh^2), \quad (2)$$

and occurs at mid-span on the side away from the loading nose.

The ratio of maximum applied flexural stress to maximum shear stress is given then

$$\sigma_{max}/\tau_{max} = 2S/h. \quad (3)$$

Thus, depending on the relative magnitudes of composite material flexural and shear strengths, and the value of the span height ratio, a specimen can fail in either shear or flexural tension.

As shown in Fig. 7, the outer fibre flexural stress at failure continually increases with increasing S/h. Thus, the flexural strength defined by testing at $S/h = 32$ is the most valid estimate of the true flexural strength. These values were 1240 MPa for the SiC-yarn reinforced PR-286 and 2410 MPa for the SiC-monofilament reinforced 5506. Examination of the high span-to-depth ratio specimens after testing indicated that the beams failed in tension at the outer fibre surface as desired. The corresponding bend moduli were 99.8 GPa for the SiC-yarn reinforced resin and 230 GPa for the SiC-monofilament reinforced resin.

The data in Fig. 8 show that the shear stress on the specimen mid-plane at maximum load increases as S/h decreases. When the condition is reached that the applied shear stress is greater than the interlaminar shear strength, the specimens will fail in shear. Observations of specimen failure modes indicated that shear failure occurred when testing at $S/h = 4$ and partial shear failure occurred at $S/h = 8$. The significant deviations of the experimental shear stress values at $S/h = 4$ from the theoretical curves of shear stress achieved assuming flexural failure, i.e., $\tau = \sigma_0/2\,(S/h)$, are consistent with the failure mode observations and indicate interlaminar shear failure occurred prior to any possible flexural failure. The interlaminar shear strengths defined by testing at $S/h = 4$ were 87.2 MPa for the SiC-yarn reinforced resin and 103 MPa for the SiC-monofilament reinforced resin. This superiority of the monofilament composites was found to be in agreement with the fact that these fibres had been surface treated. The composite flexural properties determined at room temperature are summarized in Table III.

The flexural properties were also determined at 177° C for both the yarn- and monofilament-reinforced composites, and these data are listed in Table IV. A reduction of approximately 70% in the interlaminar shear strength and a reduction of 30% in the flexural strength were observed for both composite systems. Non-linear behaviour was observed at $S/h = 32$ for both composite systems at 177° C.

3.3. Mechanical property summary

A summary of the fibre properties calculated from the composite data is presented in Table V. It is

TABLE IV Axial composite three-point bend properties determined at 177° C

Fibre	V_f	S/h	Flexural strength (MPa)	Flexural modulus (GPa)	Interlaminar shear strength (MPa)
SiC yarn	0.50	4	–	–	25.4
SiC yarn	0.48	32	797	72.5	–
SiC monofilament	0.57	4	–	–	27.8
SiC monofilament	0.57	32	1360	184	–

TABLE V Summary of fibre properties (obtained by calculation from composite data)

Source	Property	Yarn	Monofilament
Tensile data	ρ (gm cm^{-3})	2.70	3.10
Tensile data	Ultimate tensile strength (MPa)	1820	2470
Tensile data	E (GPa)	221	389
Flex data	Ultimate tensile strength (MPa)	2580	4230
Flex data	E (GPa)	208	404

evident that the mechanical properties of the SiC-yarn are similar to low-modulus graphite fibres such as Thornel 300 and consequently the mechanical properties of resin matrix composites reinforced with either fibre are relatively equivalent. There is a penalty in density for SiC-yarn reinforced composites, however, due to their much higher fibre density (2.7 gm cm^{-3} compared with 1.8 gm cm^{-3}). The SiC-monofilament reinforced composites exhibit significantly higher strength and modulus, but at a greater density penalty since the fibre density is 3.1 gm cm^{-3}. However, the flexural properties and tensile modulus are equivalent to low-modulus graphite-reinforced epoxy on a specific property (mechanical property divided by material density) basis. The SiC-monofilament reinforced composite also offers a significant improvement in compression strength.

3.4. Composite thermal expansion behaviour

The composite thermal expansion behaviour was determined over a temperature range of 20 to 170° C utilizing a single-rod quartz dilatometer referenced to a National Bureau of Standards fused silica standard. Specimens of dimensions 6.35 mm x 6.35 mm x 25 mm were heated at a rate of 2° C min^{-1} and then allowed to furnace-cool to room temperature. Specimens were cycled twice since some system equilibration generally occurs on the first cycle. A small amount of hysteresis was also observed between the heating and cooling cycles. Experience has shown that this hysteresis diminishes with slower heating rates. For these reasons, the data reported are those obtained for the cooling cycle of the second run.

The thermal expansion coefficients parallel with and perpendicular to the fibre orientation, α_0 and α_{90}, respectively, determined at 25° C and over the temperature range of 25 to 150° C are listed in Table VI. The composite expansion coefficient is greater over the temperature range due to the increase in expansion coefficient of the resin with temperature. The anisotropy in thermal expansion coefficients shown for both composite systems is significantly less than that observed for graphite-reinforced resins. For example, α_0 for high tensile strength (HTS) graphite-reinforced epoxies is typically about -0.3×10^{-6}° C^{-1} [8]. These differences in composite expansion coefficients are due to significantly different fibre expansion coefficients. An estimate of the SiC axial fibre expansion coefficients using the Halpin–Tsai relationship [9] yielded a value of 1.6×10^{-6}° C^{-1} for the yarn and a value of 2.5×10^{-6}° C^{-1} for the monofilament. In contrast, graphite fibres exhibit negative axial coefficients of expansion generally in the range of -0.5 to -1.0×10^{-6}° C^{-1}. Large differences also exist in the transverse fibre expansion coefficients. Graphite fibre is extremely anisotropic due to its structure with transverse expansion coefficients as high as 2.7×10^{-5}° C^{-1} reported for HTS fibre. In contrast, the SiC fibres used in this investigation are assumed

TABLE VI Thermal expansion coefficients

Composite	Temperature (° C)	Thermal expansion coefficient	
		α_0 ($\times 10^{-6}$° C^{-1})	α_{90} ($\times 10^{-6}$° C^{-1})
Yarn-reinforced ($V_f = 0.50$)	25	2.45	20.8
Yarn-reinforced ($V_f = 0.50$)	25–150	3.31	26.5
Monofilament-reinforced ($V_f = 0.57$)	25	2.84	19.0
Monofilament-reinforced ($V_f = 0.57$)	25–150	3.33	26.8

TABLE VII Fibre electrical resistance values

Fibre	Fibre resistance*	Voltage to arc† (V)
	HTS graphite fibre resistance	
HTS graphite	1	30
Celion 6000 graphite	4	40
Si_3N_4 coated HTS graphite	> 20 000	> 120
SiC yarn (untreated)	> 20 000	> 120
SiC yarn (surface treated)	> 20 000	> 120
SiC Monofilament	130	> 120

*Fibre tows measured over a 2.5 cm gauge length.
†120 volt maximum applied between Cu-blocks spaced 1.5 cm apart.

to be relatively isotropic. These differences do not have as great an effect on the composite transverse expansion coefficients since this parameter is primarily matrix controlled.

The thermal expansion characteristics of SiC fibres make them more compatible than graphite fibres with prospective matrix candidates. This should be beneficial to composite fabrication due to reduction in fabrication-induced residual strains.

4. Fibre electrical and thermal resistance characteristics

4.1. Fibre electrical resistance

The electrical resistance characteristics of the SiC fibres are compared with HTS and Celion* 6000 graphite fibres in Table VII. The resistance of SiC-monofilaments is approximately 130 times that of HTS graphite while the SiC-yarn has a resistance of more than 20 000 times that of HTS graphite. An arc test was also performed where fibres were placed in the gap between copper contacts, and voltage was continuously applied. As shown in Table VII, both the SiC fibres were resistant to arcing at 120 V while the graphite fibres caused arcing at 30 to 40 V.

These results are significant for two reasons. Firstly, a potential problem identified for graphite–epoxy composites is the release of graphite fibre from composites to the atmosphere during fires or explosions in the vicinity of electrical equipment [1]. This can result in electrical shorting, rendering the equipment inoperable. It is evident from the data in Table VII that this would not be a problem with SiC-reinforced epoxies, at least for electrical equipment operating at 120 V.

Secondly, the SiC fibres, in particular the SiC yarn, have very high electrical resistance values compared to graphite fibre. Because of the highly conductive nature of graphite fibres, galvanic couples can be created between graphite–epoxy and metals to which the composites are attached. In the presence of a suitable electrolyte, a differential potential between the fibres and the metal can be set up causing the metal to be anodic with respect to the fibres and resulting in corrosion of the metal structure. Such galvanic action has been considered a risk factor by aircraft manufacturers in their assessments of the use of graphite–epoxy for aircraft applications. In a recent materials development programme to assess potential composite applications in advanced commercial aircraft, it was found that the galvanic corrosion potential between graphite and aluminum was more severe than anticipated. This finding resulted in a decision to eliminate graphite–epoxy floor beams from consideration because of their intimate contact with aluminum primary structure [2]. The use of silicon-carbide reinforced epoxy would be advantageous in such applications, since the non-conducting nature of the fibre would eliminate the possibility of galvanic coupling.

4.2. Fibre oxidative stability

Graphite fibres possess relatively low oxidative stability. Extended exposure to air at temperatures above 350° C causes degradation in fibre, and therefore composite, properties. To date, this has not been a serious problem in the development of resin matrix composites. However, this is a potential problem in the future development of advanced polyimide resin systems where ultimate use temperatures can exceed 350° C. The SiC fibres, on the other hand, exhibit far superior thermal stability. It has been shown that SiC yarn is stable up to at least 500° C [5], and experience

*Trade mark of the Celanese Company.

in this laboratory in the fabrication of glass matrix composites indicated that both fibres are stable even for prolonged exposure to temperatures of 600 to 700° C [10]. It is evident that both fibres are good candidate materials for use as the reinforcement in advanced high-temperature resin systems.

5. Summary

It has been shown that SiC-reinforced resin matrix composites possess excellent mechanical properties and their use can offer some distinct advantages over the use of graphite reinforced resins. The mechanical properties of SiC-yarn reinforced resins are equivalent to low elastic-modulus graphite-reinforced resins, but at a 20% greater composite density. SiC-monofilament reinforced resins exhibit specific mechanical properties equivalent to graphite-reinforced resins, and offer the advantage of significantly higher compression strength. Both SiC fibres offer better compatibility in composites from the stand-point of thermal expansion characteristics than the graphite fibres. Finally, the SiC fibres were shown to have very high electrical resistance values, and possess significantly greater thermal oxidation resistance than the graphite fibres.

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