JOURNAL OF MATERIALS SCIENCE 31 (1996) 4395–4399

Chemical vapour deposition of silicon carbide on hollow and C-shaped carbon fibres

G. EMIG, N. POPOVSKA
Institut für Technische Chemie I, Universität Erlangen-Nürnberg, 91058 Erlangen, Germany
Y. S. LEE, B. S. RHEE
Department of Chemical Engineering, Chungnam National University, 305-764, Taejon, Korea

The thermally induced chemical vapour deposition of silicon carbide from methyltrichlorosilane (MTS) on isotropic pitch based carbon fibres with hollow and C-shaped cross sections was investigated. The uncoated and coated fibres were characterized by their mechanical properties (tensile strength, Young's modulus and torsional rigidity modulus) and surface energetic analysis. The oxidation behaviour of the carbon fibres before and after coating was discussed in terms of the weight change measured in a thermal balance during heating in an air flow at a constant heating rate.

1. Introduction

Carbon fibres are commercially produced from either a polyacrylonitrile (PAN) or a petroleum pitch precursor. Although the pitch-based fibre is relatively new to the carbon fibre market, it possesses several potential advantages over the PAN-based carbon fibre [1]. Pitch-based carbon fibre is melt spun and it has the potential to easily produce a variety of different shapes of non-circular fibre. The increased surface area to volume ratio of non-circular fibres compared to circular ones might result in increased fibre wetting through capillary action [2]. Thus, carbon fibres with non-circular shapes might provide improved fibre–matrix bonding in composites.

The use of hollow fibre is another alternative to produce composites with improved properties. It has been shown [3] that the bending stiffness of composites reinforced with hollow carbon fibres is much better than those reinforced with solid round fibres.

Therefore, carbon fibres with hollow as well as non-circular cross-sections are promising reinforcing materials for the production of advanced composites. For high-temperature applications in an oxidizing atmosphere, however, the use of a protective barrier layer is necessary owing to the sensitivity of the carbon materials to oxidation. Thin layers of silicon carbide are known to provide a good oxidation protection for carbon fibres [4, 5]. The coating is generally deposed by chemical vapour deposition (CVD). This technique affords an easy process for high rates of deposition and good control of the reaction parameters [6, 7].

In this work, hollow and C-shaped carbon fibres from isotropic pitch were coated with silicon carbide using the CVD technique. The coated fibres were characterized by mechanical properties and oxidation behaviour. Furthermore, the surface free energy of the carbon fibre surfaces before and after coating have been determined.

2. Experimental procedure

The deposition of silicon carbide from methyltrichlorosilane (MTS, CH_3SiCl_3) was performed in a resistance-heated tubular flow reactor under reduced pressure ($p_{\text{total}} = 250$ mbar) at 850 °C using hydrogen as carrier gas. Fig. 1 shows a schematic drawing of the laboratory equipment used.

As substrate, isotropic pitch-based carbon fibres with hollow and C-shaped cross-sections, manufactured on a laboratory scale by one of the authors [8], were used. The carbon fibres, as a tow (2000 monofilaments) with a length of ~15 cm, were coated with silicon carbide. The thickness of the SiC layer was determined using scanning electron microscopy (SEM).

Both, the uncoated and the coated fibers were characterized as follows.

(i) Mechanical properties (tensile strength and Young's modulus) were measured in a monofilament test with a gauge length of 30 mm and crosshead displacement of 0.5 mm min^{-1}. The cross-sectional area of the fibres was determined by embedding individual filaments in a standard mounting polyester resin, polishing the surface perpendicular to the filament axis and placing the polished sample under a microscope to photograph and to measure the filament cross-section. The torsional rigidity modulus was measured by the pendulum method described previously [9].

(ii) The surface free energy was determined by measuring the contact angle (micro-Wilhelmy technique) of a variety of liquids with known polar and dispersive components of their total surface energy,

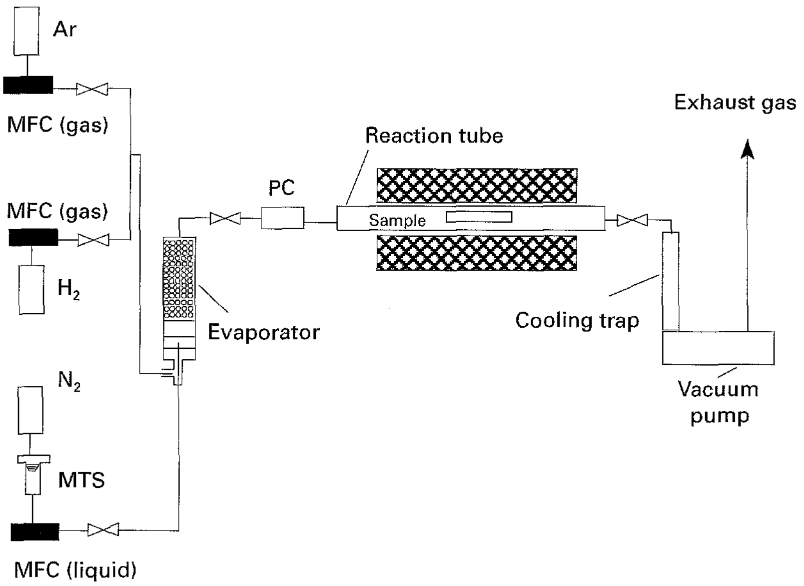

Figure 1 Schematic drawing of the CVD laboratory-scale equipment. MFC, mass flow controller; PC, pressure controller; MTS, methyltrichlorosilane, CH_3SiCl_3.

TABLE I Characteristics of isotropic pitch-based carbon fibres (CF) with round and non-round cross-sections

Property	Round CF	Hollow CF	C-shaped CF
Diameter (μm)	25	–	–
Cross-sectional area (μm^2)	491	1180 ± 261	385 ± 117
Density (g cm^{-3})	1.73	1.69	1.71
Tensile strength (MPa)	932 ± 167	401 ± 93	836 ± 285
Young's modulus (GPa)	55 ± 4.4	35.5 ± 8	92 ± 20
Torsional rigidity modulus (GPa)	5.1	12.5	12.1

and analysing the results according to the method proposed by Kaelbe [10]. The liquids used included water, ethylene glycol, glycerol and bromonaphthalene. Ten single-filament samples were measured for each wetting liquid and fibre.

(iii) Oxidation behaviour was measured in a thermal balance and expressed as the weight change during heating in air flow with a constant heating rate of 5 K min^{-1}. The reinforcing behaviour of the uncoated carbon fibres with round, hollow and C-shaped cross-sections in an epoxy matrix was estimated by measuring the interlaminar shear strength (ILSS) [11], flexural strength and flexural modulus [12, 13] of the epoxy composites (60 vol % carbon fibre).

3. Results and discussion

3.1. Characterization of isotropic pitch-based carbon fibres with round, hollow and C-shape cross-sections

3.1.1. Mechanical properties

The mechanical properties of the uncoated fibres are presented in Table I. The tensile strength and Young's modulus are relatively low due to the isotropic structure of the carbon fibres. The torsional rigidity modulus depends strongly on the shape of the fibre cross-section. Hollow and C-shaped carbon fibres show a value for the torsional rigidity modulus more than twice as high as compared to the round fibre.

3.1.2. Reinforcing behaviour in epoxy composites

The characteristics of commercially available epoxy resin/hardener systems reinforced with carbon fibres with round, hollow and C-shape cross-sections are presented in Table II. The adhesion between fibre and matrix has been estimated by interlaminar shear strength measurements with the short beam test [11]. As can be clearly recognized from Table II, the adhesion between the C-shape and the hollow carbon fibre and epoxy resin is better than by the round fibre and this is due to the higher surface free energy of these fibres, resulting in an improved wettability by polar substances. Thus, the reinforcing effect of the hollow and C-shaped carbon fibres, expressed as flexural properties of the corresponding epoxy composites, is found to be more than twice as high compared to the traditional round fibre.

3.2. Modification of the carbon fibre surface by coating with SiC

The deposition of silicon carbide from methyltrichlorosilane (MTS) proceeds in a hydrogen atmosphere, according to the overall equation

$$CH_3SiCl_3(g) \xrightarrow{H_2} SiC(s) + 3HCl(g) \qquad (1)$$

If the substrate for the CVD is a fibre bundle consisting of individual monofilaments, the processes of mass

TABLE II Characteristics of epoxy resin reinforced with isotropic pitch-based carbon fibres (CF) with round and non-round cross-sections

Property	Round CF	Hollow CF	C-shaped CF
Surface free energy of the fibre (mJ m^{-2})	39.6	43.3	58.7
Interlaminar shear strength (ILSS) (MPa)	8.3	9.6	12.5
Flexural strength (MPa)	114	203	256
Flexural modulus (GPa)	0.62	1.33	1.65

transfer from the bulk gas phase to the outer surface of the bundle, transport of the precursor into the bundle and the chemical reaction on the surface of the individual monofilaments, take place simultaneously. Therefore, a uniform coating of the individual monofilaments in a bundle can be expected only if the overall process is controlled by the rate of the chemical reaction, and not by the mass transfer of the reactants.

The details of the mathematical description of the CVD of silicon carbide from MTS on a carbon fibre bundle will be described in a separate paper. Using this mathematical model, the deposition parameters (temperature and pressure) for a uniform coating of the monofilaments in a fibre bundle can be calculated. A deposition temperature of less than 900 °C at 250 mbar total pressure was found to be optimal for the bundle geometry of the carbon fibres investigated.

Thus, the chemical vapour deposition of silicon carbide from MTS on the carbon fibres was performed at 850 °C under reduced pressure of 250 mbar and mole fraction of the educt in the gas phase 0.6. The adhesion between fibre and coating was found to be very good, as indicated in the scanning electron micrographs.

3.2.1. Mechanical properties of the coated fibres

The results of the measurements of the mechanical properties of the uncoated and coated isotropic pitch-based carbon fibres are presented in Figs 2–4 in terms of the tensile strength, Young's modulus and torsional rigidity modulus as functions of the layer thickness.

The tensile strength of the carbon fibres is strongly negatively influenced by the SiC-layer. This effect has to be explained in terms of differences in the coefficient of thermal expansion, as well as different mechanical properties of fibre and coating. Therefore, a layer thickness of more than 100–150 nm seems to be unacceptable, because of the strong decrease in the initial tensile strength.

As a contrast, the influence of the SiC coating on the Young's modulus of the carbon fibres is very weak. The difference in the stiffness of ceramic materials and carbon fibre is too significant, so that the coating takes over all the applied stresses.

An increase in the values for the torsional rigidity modulus has been found for the coated fibres and this effect is strongly marked in the case of the hollow fibre.

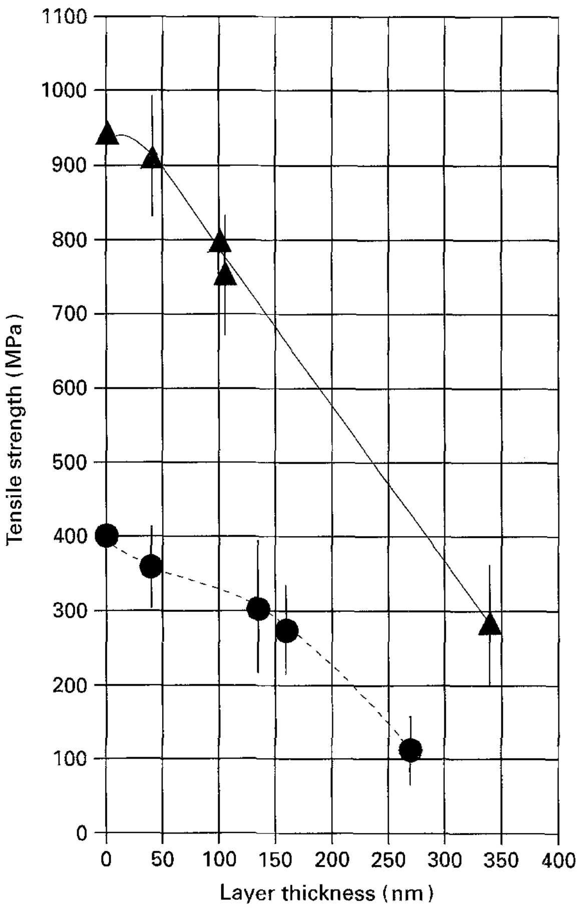

Figure 2 Tensile strength of isotropic pitch-based carbon fibres with hollow and C-shaped cross-sections, as-received and coated with silicon carbide.

3.2.2. Surface energy analysis of the coated fibres

It is well known that for the transfer of fibre properties to the composites, a good wettability of the fibre surface by the matrix is required [14]. The surface free energy of the traditional round carbon fibres is very low, so that they are poorly wetted by polar substances [10]. The increased surface area to volume ratio of non-circular fibres results, as shown previously, in increased fibre wetting through capillary action [15].

The surface free energy of the carbon fibres before and after coating with silicon carbide is presented in Fig. 5. As shown previously, the uncoated carbon fibres produced from isotropic pitch exhibit a much higher surface free energy than the fibres with the same cross-section produced from mesophase pitch [15]. This effect can be explained by the sensitivity of the isotropic pitch precursor to oxidation during the spinning process and by the disordered isotropic microstructure of the corresponding carbon fibres.

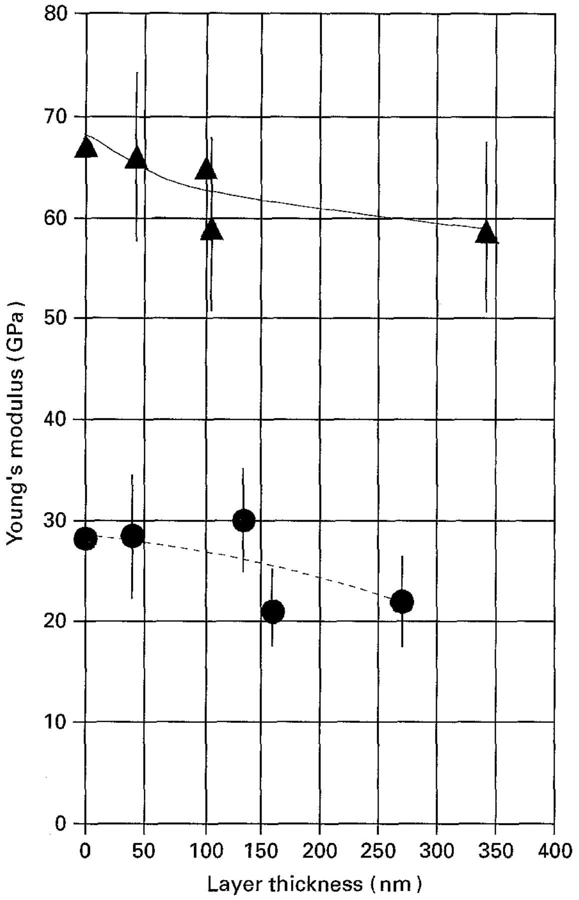

Figure 3 Young's modulus of isotropic pitch-based carbon fibres with (●) hollow and (▲) C-shaped cross-sections, as-received and coated with silicon carbide.

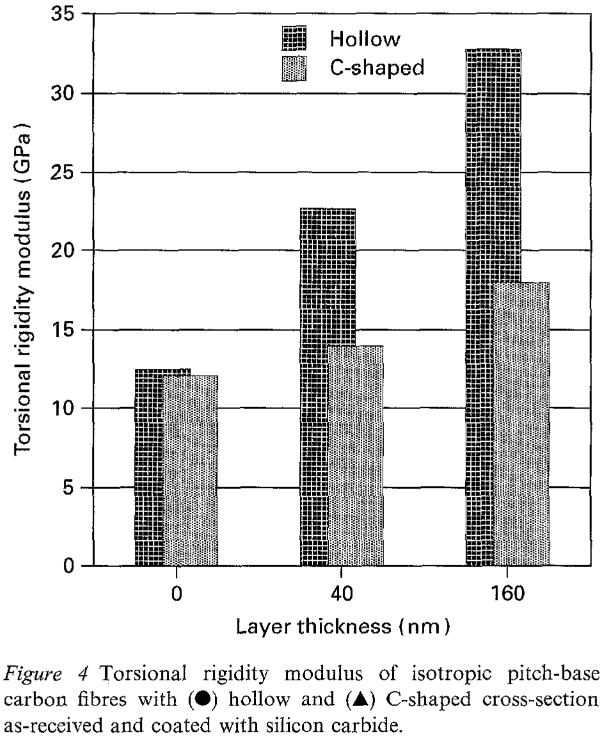

Figure 4 Torsional rigidity modulus of isotropic pitch-based carbon fibres with (●) hollow and (▲) C-shaped cross-sections, as-received and coated with silicon carbide.

The deposition of silicon carbide does not significantly affect the surface free energy of the isotropic pitch-based carbon fibres. Therefore, the coated fibres will also be well wetted by polar substances, which is a precondition for improved fibre–matrix adhesion in composites.

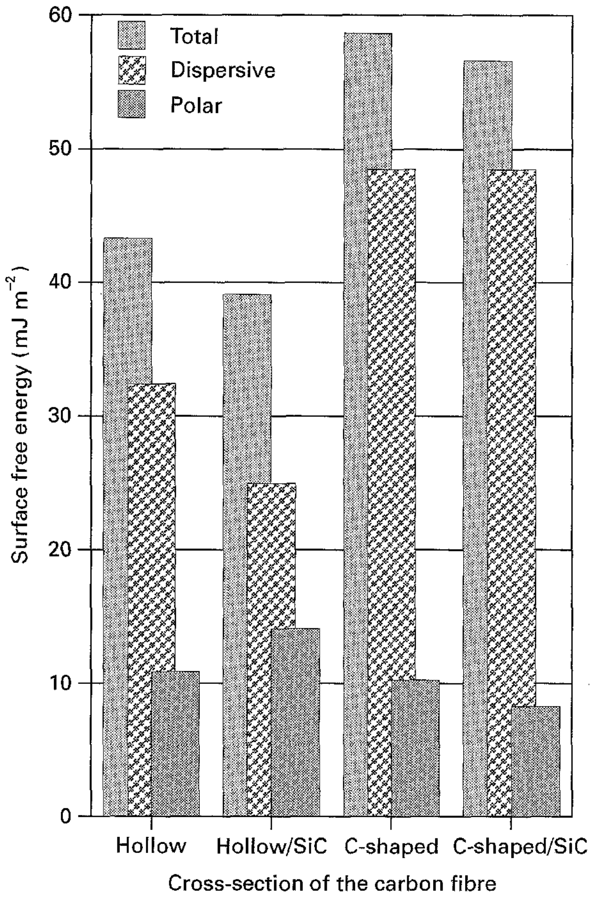

Figure 5 Surface free energy of isotropic pitch-based carbon fibres with hollow and C-shaped cross-sections, as-received and coated with silicon carbide (100 nm).

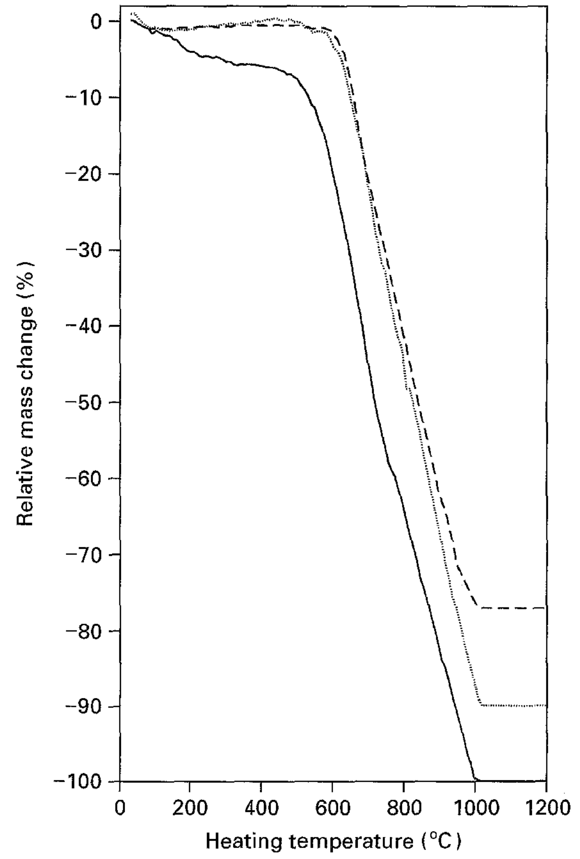

Figure 6 Relative mass change of isotropic pitch-based carbon fibres with (···) hollow and (– – –) C-shaped cross-sections, (——) as-received and (– – –, ···) coated with silicon carbide (100 nm) (heating rate $5\ \mathrm{K\,min^{-1}}$, air flow).

3.2.3. *Oxidation behaviour of the carbon fibres after coating with SiC*

The results of the oxidation tests are shown in Fig. 6 in terms of the relative mass change as a function of the heating temperature. The samples, carbon fibres with hollow and C-shaped cross-sections coated with 100 nm SiC-layer as well as the uncoated fibres, were heated in a thermal balance with a constant heating rate of 5 K min^{-1} in an air flow.

There is a considerable mass loss for all the samples investigated. The coating with SiC, however, leads to shifts in the temperature for the start of the burn off and the residual mass at 1200 °C to higher values. The form of the curves in Fig. 6 leads to the conclusion that the oxidation of carbon fibres is strongly slowed down by coating with 100 nm of silicon carbide.

4. Conclusions

1. The isotropic pitch-based carbon fibres with hollow and C-shaped cross-sections provide improved fibre-matrix bonding in epoxy composites owing to their high surface free energy. As a result, the reinforcing effect in composites with epoxy matrix increases significantly compared to the traditional round fibres.
2. The deposition of a thin layer of silicon carbide (100–150 nm) by the chemical vapour deposition technique does not significantly affect the tensile strength and Young's modulus of the fibres. However, the torsional rigidity modulus increases strongly after coating.
3. Using a mathematical model, the deposition parameters of the CVD process for a uniform coating of the monofilaments in the fibre bundle with SiC from methyltrichlorosilane (MTS), can be calculated.
4. By coating the carbon fibres with SiC, the oxidation process starts at higher temperatures and the rate of burn off is slowed down.
5. The coated carbon fibres with hollow and C-shaped cross-sections are well wetted by polar substances. Thus, they seem to be promising alternative reinforcing materials for high-temperature applications in the production of advanced composites.

Acknowledgements

The authors thank the German Research Foundation (DFG-project Em 31/3-2) and the Korea Science and Engineering Foundation (KOSEF) for financial support.

References

1. D. EDIE, E. FITZER and B. RHEE, in "Proceedings of the Verbundwerk 1991", edited by S. Schnabel, Demat Exposition Managing, Frankfurt, Wiesbaden, 1991, p. M 8.3.
2. D. D. EDIE, N. K. FOX, B. C. BARNETT and C. C. FAIN, *Carbon* **24** (1986) 477.
3. G. NIEDERSTADT, *Z. Flugwiss. Weltraumforsch.* **8** (1) (1981) 30.
4. E. FITZER and G. SCHOCH, in "Proceedings of the 4th International Conference on Carbon", Baden-Baden (1986) p. 856.
5. G. EMIG, N. POPOVSKA and G. SCHOCH, *Thin Solid Films* **241** (1993) 361.
6. J. SCHLICHTING, *Powder Metall. Int.* **12** (1980) 141.
7. *Idem, ibid.* **12** (1980) 196.
8. B. RHEE, *High Temp. High Press.* **22** (1990) 267.
9. C. W. KIM, in "Material Mechanics" (Seoul, Korea, 1978) p. 123.
10. G. E. HAMMER and L. T. DRZAL, *Appl. Surf. Sci.* **4** (1980) 340.
11. ASTM-D-2344-76, DIN 29 971 (American Society for Testing and Materials, Philadelphia, PA).
12. DIN 29971 (07.1986), Unidirektionalgelege – Prepeg aus Kohlenstoffasern und Epoxidharz. Technische Lieferbedingungen (July, 1986).
13. DIN 53457 (10.1987), Prüfung von Kunststoffen. Bestimmung des Elastizitätsmoduls in Zug-, Druck- und Biegeversuch (October, 1987).
14. J. MATSUI, *Crit. Rev. Surf. Chem.* **1** (2) (1990) 71.
15. G. EMIG, N. POPOVSKA, D. D. EDIE, B. S. RHEE, in "Extended Abstracts Carbon 94", 3–8 July 1994, Granada, Spain, p. 714.

Received 1 December 1994
and accepted 13 February 1996