

THE PRODUCTION OF HOLLOW CARBON FIBRE FROM A SPECIAL PAN PRECURSOR

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SUMMARY:

Since carbon fibres were first produced in the 1960s, considerable advances have been made in improving their mechanical properties and those of their composites. Tensile strengths can now exceed 5GPa and, for different fibres, moduli in excess of 600GPa are achieved. These have not been accompanied by comparable improvements in compressive properties, because failure in composites is determined by buckling criteria. Large diameter hollow carbon fibre has the potential to achieve significant improvements in compressive strength; to improve damage tolerance and, possibly, serve as a “smart” material or in medical applications.

MSS /DERA has developed a technique for spinning hollow PAN precursor fibres and converting them into useful carbon fibre. Although consistency in fibre structural morphology has been difficult to attain, the constituent carbon is found to be similar to that of high strength carbon fibre. Simple mechanical testing has, however, revealed that although comparable modulus can be realised, the Ultimate Tensile Strength (UTS) is lower. This is believed to be a consequence of flaws/inhomogeneities and the lack of structural homogeneity within filaments. Even with such experimental fibres, preliminary compression testing indicates higher strain to first failure in comparison with a commercial fibre.

KEYWORDS: Carbon fibre, compression, processing, hollow

INTRODUCTION

The first carbon fibres were produced in the nineteenth century by carbonising cotton threads for use as the incandescent filaments of the early light bulbs of Edison [1] and Swan [2]. However, it was only in the 1950's when graphite whisker single crystals were produced with high tensile moduli and strengths, that carbon fibres showed potential as structural reinforcements. The basis for this was the carbon-carbon bond which, in three dimensions, is the strongest of all bonds. In its crystalline forms as graphite and diamond, carbon also has, in certain crystallographic directions, the largest known stiffness. These properties, combined with graphite's relatively low density, indicated very high specific strengths and moduli for carbon fibre.

Research, primarily in Japan, the U.K. and the U.S.A. sought a suitable precursor fibre and appropriate route for conversion to achieve the best properties as many forms of carbon fibre can be produced which have neither high strength nor high modulus. This was realised in the 1960's with the development of conversion processes for polyacrylonitrile (PAN) fibres [3-5]; some of which [7-10] was performed at the Royal Aircraft Establishment (RAE), the forerunner of DERA. Carbon fibre has subsequently been produced from a number of other materials including pitch [11-13], coal [14], polyethylene[15], lignin-polyvinyl alcohol mixtures [16] and the vapour phase [17-21]. However, only three precursors have achieved any commercial significance: rayon, PAN and pitch. Of these, production from the former has largely ceased and ex-PAN carbon fibres dominate the market for composites.

Since its development, there have been great improvements in the tensile properties of carbon fibre which have been realised in the widespread use of carbon fibre reinforced composites. Yet although the tensile strength of carbon fibre has been doubled during the last decade or so, its compressive strength has remained essentially unchanged. This is problematic because the intrinsic fibre compression strength has a direct influence on composite properties. Consequently, the compression strength for composite structures is usually little more than half that in tension and sometimes much less. As compressive failure is the design-limiting criterion for many components, such as aircraft wings, a number of studies have been performed in an effort to understand its mechanism and thereby offer options for improvement. There remains some debate over the actual mechanism. Buckling or kinking has been observed [22-24] but also shear failure [22,24-27].

Shear failure is observed for high modulus fibres [22] and is the mechanism of failure for pitch fibres [24,25]; probably because of the specific microstructure of pitch based fibres which makes them susceptible to shearing forces during compression[24,27]. Kinking/microbuckling appears to be the failure mechanism for lower modulus fibres [22] and for PAN-based fibres[24], although contradictory evidence has been presented[26]. It has been suggested that buckling is due to the two-phase structure of high strength PAN-based fibres and as a consequence of greater disorder [24]. It also seems clear that for a comparable tensile modulus, PAN based fibres have a higher compressive strength than pitch based [28] and that compressive strength [28] and failure strain [27] increase with decreasing tensile modulus.

If carbon fibres with higher compressive strengths could be produced, there would be a consequent improvement in the compressive properties of their composites. Such an advance would be particularly beneficial for improved aircraft performance.

In principle, fibres of larger diameter may facilitate these developments by providing a larger cross-sectional area and therefore greater resistance to buckling. This is not possible because from the main method of manufacturing (that is the conversion of PAN precursor fibre), there is an upper limit of about 10µm on the diameter. During conversion, product gases are produced and have to diffuse out of the fibre. If the fibres are too large, this cannot take place and conversion is incomplete. Structure mechanics shows that the removal of material from the neutral axis facilitates improvement in resistance to compressive loads, for the critical buckling load is proportional of the structure's moment of inertia. A cylinder is thus more resistant to compression loading than a solid column.

For an ideally straight, axially loaded column with no restraint at the ends, Euler's expression states that the critical load, P_{crit} at which a column of length L will buckle is proportional to its moment of inertia, I :

$$P_{crit} = \frac{\pi^2 EI}{L^2}$$

Where E = modulus of elasticity.

As a cylinder has a higher moment of inertia than a solid column, by analogy, hollow carbon fibre would offer similar microstructural advantages when utilised in composite materials; provided that the failure is by buckling. This has been indicated by Niederstadt's work. [29].

Hollow carbon fibre composites offer particular advantages to aircraft. Extensive use may lead to significant reductions in weight, and improvements in agility, range and payload. Furthermore, the impact strength should be improved as the hollow fibre will increase the shock absorption capacity of the composite. There is also the potential to incorporate a third phase into the centre of the hollow fibre in the field of "smart" materials and possibly applications for medical technology where filtration may require the high selective adsorption of carbon surfaces.

The main objective of this work has been to produce hollow carbon fibres with the potential for structural reinforcement. This paper describes initial work in the process to achieve this goal.

Practical considerations

As PAN-based carbon fibre dominates the market for structural materials and hollow pitch-based carbon fibre is known [30-33], the Mechanical Sciences Sector (MSS) at DERA decided to pursue the production of hollow carbon fibre from a PAN precursor. This presented two major challenges:

- i) producing hollow PAN precursor fibre; and
- ii) converting the aforesaid fibre into useful carbon fibre.

Production of hollow PAN precursor

To produce a polymer fibre, the polymer has to be *spun*. Melt spinning is preferred if the polymer can be melted without degradation and is a common method for spinning thermoplastics. Dry spinning and wet spinning involve the dissolution of a polymer into an appropriate solvent to form a polymer dope. The former involves the extrusion of the dope into a heated zone to evaporate solvent, whereas for the latter the fibre is spun into a liquid bath containing a solvent/non-solvent mixture called the coagulant. The solvent is nearly always the same as that used in the dope and the non-solvent is usually water.

There already exists technology for producing hollow polymeric fibres and specifically, hollow PAN fibres. However, most of that for PAN concerns the manufacture of large diameter porous walled filaments, e.g. for medical applications [34,35], which are unsuitable for conversion into useful carbon fibres. Fitzer [36] addressed this problem through a unique melting process (akin to his work on pitch-based fibre [37] whereby a c-shaped filament collapses inwards to form a hollow fibre) but melt spinning is not employed for commercial precursor fibre production – it is via wet-spinning.

Through the efforts of the late James Ferguson and his co-workers at the University of Strathclyde, a patented process for producing a hollow PAN precursor for carbon fibre has been developed. This makes use of a process known as *dry-jet wet spinning*, which is a combination of dry and wet-spinning. Polymer dope is extruded into an air gap before entering the coagulation bath containing a mixture of solvent and water. This method helps prevent coagulation and the air gap has been shown to produce fibres that are stronger and more extensible than fibres produced from an immersed jet. It has also been associated with the alignment of molecular chains prior to coagulation. When the polymer enters the coagulation bath a phase inversion takes place to produce a solid fibre. This is the most critical process.

The transition from liquid to solid may take place via two routes: phase inversion and gelation. The former is the precipitation of polymer to form a solid phase and is preferable for membrane-type fibres (e.g. for use in medical applications). The resulting fibre is essentially a swollen gel, is unoriented and has a microstructure consisting of a fibrillar network with the spaces in-between called macrovoids. Such fibres have poor mechanical properties and are unsuitable precursor fibres. The best combination of tensile properties is achieved through gelation when the fibre has a homogeneous, dense gel structure with small fibrils and no macrovoids. This is controlled by the degree of

solvent concentration in the coagulation bath and its temperature. The precursor diameter is ultimately controlled by the size of hole through which the dope is extruded, but also by post extrusion stretching and drawing. Careful control of these parameters facilitated a precursor fibre that was suitable for processing into carbon fibre. The process requires further work as the precursor fibre is still of inconsistent quality. This is presently being addressed to enable the benefits of hollow carbon fibre to be properly assessed.

Production of carbon fibre from a PAN precursor is a three stage process comprising oxidation (or stabilisation), carbonisation and graphitisation. Oxidation involves heating the fibre between 200°C and 300°C where the open chain structure of PAN is converted into a closed “ladder” chain. Although the stabilisation process can be carried out in an inert atmosphere, the usual procedure is for heating in an oxygen environment, often air, which facilitates a more rapid, higher yield conversion, hence the more usual descriptor “oxidation”. The fibre is also tensioned to produce stretching and alignment.

The carbonisation stage involves the evolution of H₂, NH₃, HCN and N₂ so that by 1000°C only a small percentage (less than 5%) of substituted nitrogen remains. The fibre is now almost completely carbon. Further heating beyond 1000°C in an inert atmosphere (the graphitisation stage is usually between 1300°C - 3000°C) achieves a better stacking of the constituent carbon layer planes within the carbon fibre structure and any remaining nitrogen is driven off. The resulting carbon fibres consist of non-graphitic carbon [38] which has two dimensional long range order consisting of carbon atoms in planar hexagonal networks, as with graphite, although often with vacancy-cluster defects.

In order to realise the potential of hollow PAN fibre as a precursor for carbon fibre a suitable conversion process was required. DERA has set up a pilot processing plant consisting of a four-zone oxidation oven; a five-zone carbonisation furnace and a high temperature furnace.

Precursor formulations and processing conditions are usually proprietary or remain undisclosed, which hinders the optimisation of the process. To achieve this, commercial precursor, Courtaulds 6k tow SAF (Special Acrylic Fibre), was processed under a variety of conditions to enable carbon fibre properties to be tailored to specific needs. The temperatures, tension and rate of throughput were altered until a “standard” processing regime was established which gave carbon fibre with properties similar to a commercial fibre. The fibre chosen was Toray Industries T300, possessing a tensile strength of 3.53GPa and modulus of 235GPa from manufacturer’s data (Table 3) and in-house measurements of 3.21GPa and 243GPa respectively (Table 3). When DERA carbon fibre was produced with similar properties (tensile strength and modulus of 3.03GPa and 245GPa respectively Table 3) the selected conditions would serve as a useful starting point for subsequent fibre processing.

Oxidation is probably the most crucial step in processing because of the subsequent effect on carbon fibre properties [39-44]. The application of tension is crucial to prevent shrinkage (which would otherwise lead to degradation of properties); the heating rate

must be controlled because of the large exotherms involved; and the reaction kinetics depend critically on fibre diameter (for the diffusion of gases), polymer composition and other process parameters such as air flow oven configuration etc. [5,40,41,45,].

The initial quantities of precursor fibre precluded use of the pilot plant and bench scale facilities were commissioned. These consisted of a single zone oxidation oven, a three-zone carbonisation furnace and a single zone high temperature furnace. The conditions prevalent within the pilot plant oxidation oven had facilitated production of carbon fibre with reasonable mechanical properties (Table3). To achieve a comparison with the single zone bench scale oven, a method of monitoring the process was required.

The degree of cyclisation for oxidised fibre can be determined by shrinkage because the shrinkage of PAN fibre during oxidation is related to the degree of oxidation e.g. 24% shrinkage corresponds to 50% cyclisation [47,48]. However, the usual way is by the Aromatisation Index. This was introduced by Uchida et al [49] and compares the wide angle x-ray diffraction patterns of unoxidised and oxidised PAN fibres. The Aromatisation Index (AI) is defined by:

$$AI = I_A / (I_A + I_P)$$

Where I_A = intensity of the diffraction peak at $2\theta \approx 26^\circ$
 I_P = intensity of the diffraction peak at $2\theta \approx 17^\circ$

Preliminary studies were performed but highlighted a number of drawbacks for continual monitoring:

- i) a direct comparison of the intensity is not possible because the number of fibres scanned in each sample was not identical
- ii) intensities are not directly measured from the particular software used; and
- iii) it proved very labour intensive and, therefore, is not well-suited for continual monitoring of process conditions.

An alternative method, developed and successfully utilised by Tsai [47,50-52] was, therefore, used which is simpler; less labour intensive and allows the study of a larger number of samples.

The process of oxidation for PAN is exothermic, so the temperature at the onset of the exotherm is the temperature of acrylonitrile cyclisation. The exothermic heat is mainly attributed to the cyclisation of the acrylonitrile units so that the greater the cyclisation for PAN fibre, the lower the exothermic heat for oxidised PAN. AI can, therefore, be calculated using Differential Scanning Calorimetry (DSC):

$$AI = (H_V - H_O) / H_V$$

where H_V = the exothermic heat of virgin PAN and
 H_O = the exothermic heat of oxidised PAN

Tsai's work has established a close correlation between AI calculated by the DSC method and that by x-ray diffraction [47]. A similar correlation was found here and it was decided to use Tsai's method for calculating AI to enable monitoring of the stabilisation process.

It has been established [10,53,] that it is undesirable to cyclise/aromatise (i.e. produce a closed structure of) more than 50% of the PAN as there is a consequent reduction in the mechanical properties of the resultant fibres [42]. Alteration of oxidation conditions had produced an AI of 37% (Table 1), which correlated to the properties of DERA carbon fibre (Table 3). A comparison of dwell times and temperatures resulted in a comparable temperature of 230°C and dwell time of one hour (Table 1).

Preliminary production of hollow carbon fibre was carried out using the bench-scale apparatus and mechanical properties were low. With the production of larger quantities of hollow PAN precursor it has been possible to use the pilot plant carbonisation and heat treatment furnaces. However, it has not yet been possible to produce the lengths of fibre required for use of the pilot plant oxidation oven and the bench-scale oxidation oven has been extensively used.

Structural examination

The morphology of carbon fibre is established from that of the precursor so that any lack of structural homogeneity in hollow PAN precursor is observed in hollow carbon fibre. This has proved to be one of the most difficult challenges, for considerable variation in fibre outer diameter, wall thickness and centrality of lumen have been observed. Such variations in the precursor fibre can hinder/ prevent conversion to carbon fibre and in the final product provide inconsistent properties. Fig1 illustrates a lack of uniformity in wall thickness which has led to a collapse of the fibre into a c-shaped cross section. Fig2 contrasts a similar fibre with one of a more uniform wall thickness and central lumen. However, the lumen is non-circular thereby providing points of stress concentration. Fig3 indicates the considerable variation with some fibres. The "seam" that is visible in three fibres, is a direct consequence of the coagulant being injected into the polymer dope (as it is extruded into the air gap) at an angle. The dope is then unable to form a uniform wall thickness so that during carbonisation, a split is formed along part of the fibre's length as material shrinkage occurs. Although the morphology of the fibres is inconsistent, the conversion process appears complete from an examination of the constituent carbonaceous material. Fig4 shows the detail of a cross-section illustrating a granular morphology . This is typical of high strength carbon fibres [24,28,54,55] and is consistent with observations for high compressive strength fibres. [56]. A cursory examination of hollow fibre using laser Raman spectroscopy and TEM provides corroborating evidence.

The former has proved useful for examining the degree of disorder within carbonaceous materials. For a graphite crystal only one first order Raman band is observed [57] which is the main line of scattering in all graphite structures [58]. This has been accurately situated at 1580cm^{-1} [57] although some variation is recorded in its position [58,59]. As

this line is characteristic of graphitic materials it is also known as the G-line. In less perfect graphitic materials with lattice disorder and a reduction in crystallite size, other contributions to the Raman spectrum are observed. In some forms, including carbon fibre a band, centred at about 1360cm^{-1} termed the D-line (for disorder) is observed. The exact position of this band is far less certain than the G-line, which is reflected in the variety of reported values [57-60] - values from 1354cm^{-1} to 1362cm^{-1} have been noted for carbon fibres.

Tuinstra and Koenig [61] and following them other workers [60,62-65] have shown a linear relationship between the ratio of intensities of the two lines I_D/I_G (as estimated by Laser Raman Spectroscopy) and the reciprocal of the near crystallite diameter in the (graphite plane) direction $1/L_a$, with L_a estimated by x-ray diffraction. This ratio has also served as a measure of disorder [66,67].

Illustrative first order spectra from T300 and DERA hollow carbon fibre are shown in Fig5 and the average intensity ratio shown in Table 2. This suggests that the degree of structural ordering within hollow carbon fibre is similar to that observed within commercial, T300 fibre and that the processing regime employed at DERA is adequate for replicating a commercial process. TEM studies were performed on longitudinal specimens (prepared by argon ion milling) using a Philips 300 kV microscope. There was some variation in ordering along the fibre's length. Some areas (Fig6) gave diffraction patterns and lattice fringe images similar to high strength fibres [68] whereas others were less oriented (Fig7). These observations indicate that the material constituting the hollow carbon fibres is similar to that forming typical high strength fibres. The variation in morphology and ordering along individual filaments however, may prevent the material's mechanical properties being realised.

Mechanical testing

Some considerable expertise has been developed at DERA (formerly as RAE) in the field of single testing since the production of the first carbon fibre and it was felt that this would offer a straightforward means of measuring tensile properties. Consistency in properties for commercial and DERA solid carbon fibre had been achieved with a sample population of 20. Due to the lack of consistency of hollow fibre it was decided to test a minimum of 100 filaments to achieve a more representative profile of tensile strength and modulus. Weibull statistics have been applied to the resulting data and are presented elsewhere[69]. The data presented here is for illustrative purposes only.

The procedure followed is similar to that of ASTM D33-79. With extreme care, single filaments were selected at random from a fibre tow and affixed across a thin cardboard tab containing two slots. The first slot, oval in shape, provides a 25mm gauge length for tensile testing and the second, a circle, provides a 10mm gauge length for diameter measurement. Each fibre is positioned centrally across both gauge lengths and aligned parallel to the longitudinal axis of the tab. The fibre is securely positioned using an adhesive and the tab cut to allow use of the frames. Diameter measurements are taken optically.

The frame containing the larger gauge length is grasped in the upper jaws of an Instron 1122 Test machine and lowered to the stationary jaws. Alignment is visually checked before the lower jaws are tightened. The side supports are then burnt away using an electrically heated wire and the specimen tensioned using a 10N load cell at a cross-head speed of 0.1mm/sec. The load and extension are taken from a chart recorder and it is then a simple matter to calculate tensile strength, modulus and strain to failure. To determine wall thickness hollow fibres are mounted in Ciba-Geigy's MY750 epoxy resin, with methyl nardic anhydride as the hardener and K61B as accelerator – 100:90:4 pbw respectively. The sample is ground and polished to reveal the fibre cross-section and optical photomicrographs taken of each sample. Four readings at 90° are taken for each fibre so as to lessen the effects of non-circular wall thickness and non-uniform diameter

Preliminary hollow carbon fibre exhibited low UTS, of about 0.4GPa (Table 1) and a low modulus, of about 107GPa (Table 3). Improvements have been made in the processing which has resulted in increased values for both, to 0.52GPa for UTS and 249GPa for modulus. The value for modulus is comparable with both T300 and in-house solid carbon fibre, which is heat treated under similar conditions. The structural examination suggests that the ordering of the constituent carbon material in hollow carbon fibres is similar to high strength fibres, yet tensile strength remains low. Modulus is a material property, whereas UTS is sensitive to flaws and misaligned planes [70-74] and there are two possible sources – the fibre's morphology and the constituent material itself. It is clear (Figs 2,3) that there can be wide variations in fibre morphology which will adversely affect the fibre properties and contribute to the large standard deviations noted. Even if the constituent carbon has the same order as that of high strength fibres, a hollow fibre possesses two surfaces (internal and external) and an increased volume of material per unit length. For example, for a hollow carbon fibre of an assumed wall thickness of 7µm and outside diameter of 35 µm, in a 25mm gauge length there is 25 times the volume of material as in a 7µm diameter solid fibre. This increases the likelihood of critical defects. This may prevent hollow carbon fibre from ever approaching the tensile strengths of solid fibres with comparable moduli. A possible improvement may lie in increasing the degree of order within the hollow fibre thereby reducing the number of defects and misorientations. This approach is itself flawed for a higher modulus corresponds to a low tensile strength and lower compressive properties.

Preliminary compression testing

The small quantities of hollow carbon fibre initially produced has precluded scale-up to compressive testing of composites using standard composite test procedures. Preliminary testing was therefore confined to single filaments and small numbers of fibres. Although such testing is severely limited in its usefulness, and by its very nature may offer only qualitative indications, it was felt that this may prove a useful indicator in the development of improved compressive properties, highlight possible areas of improvement in processing and facilitate a comparison with a commercially available fibre T300. Similar studies by others have employed a number of different test methods including:

- i) the critical fibre length[9];
- ii) the compression test of single fibre composites[10];
- iii) the cantilever beam test [11, 12];
- iv) the elastica loop test [13-15]; and
- v) the tensile recoil test[16-18].

Of these, it was felt that the most minor disadvantages were from embedding a fibre in resin. For example, interpretation of results from the elastica loop test and cantilever beam are complicated because failure can be either tensile or compressive. The tensile recoil test can provide compressive strength rather than strain values, but the deformation rates used are uncontrollable and extremely high. The main drawback in compressing single fibre composites are visually observing the failure, as it may occur anywhere along the fibre length and determining the extent of residual compression in the filament due to matrix shrinkage; although the latter can be reduced to a minimum by a careful curing regime.

Initial testing has been only partially successful. Fibre has been embedded in epoxy resin (Hexcel laminating resin LY5052 with hardener HY5052) columns of three cross-sections – U, H and circular, and of lengths to 70mm. Testing has been performed on an Instron 1122 test machine with the first failure noted through cross-polarised light.

Buckling of the larger samples prevented the recording of any useful data and small samples (10mm gauge length) gave anomalously high values for first strain to failure (in excess of 5%) although a consistent improvement of hollow fibre over T300 was noted; on average the first failure occurring at 7% higher strain. Until detailed testing is performed, we attach little significance to these results.

CONCLUSIONS

The production of a hollow carbon fibre from a solution spun hollow PAN precursor has been successfully demonstrated. Altering the heat treatment regime can vary the UTS and tensile modulus with a comparable modulus to a commercial fibre being achieved. Some control has also been gained over the tensile strength, but the actual values remain low - hollow fibre produced via conversion process comparable to that for high strength fibre have a similar modulus but only one-third the UTS. As UTS is flaw sensitive, it is suggested that this may be a direct consequence of greater numbers of flaws/inhomogeneities within the fibre and its general lack of structural uniformity. The former may be addressed by further filtration of the spinning dope and clean room conditions. The latter is dependent on the precursor fibre.

There is a clear variation in filament structure, as seen in the non-uniform wall thickness and non-central lumen. These arise from the spinning process. Coagulant is injected into the dope stream via a needle and if its position is altered, the coagulant is injected at an angle. The off-centre lumen and variable wall thickness result. The initial spinneret design was such that the injecting needle position was altered by the flowing dope. This flaw has since been rectified so that the needle has the required rigidity to resist distortion. Spinning with a redesigned spinneret is ongoing.

If fibre of a more uniform structure and less flaws is produced, it will be possible to accurately assess the mechanical properties and reinforcing efficiency of hollow carbon fibre. However, as has already been noted, the UTS may never approach that of solid fibres with comparable moduli because of the greater volume of material per unit length.

ACKNOWLEDGEMENTS

This work forms part of Technology Group 4 (Materials and Structures) of the UK MOD Corporate Research Programme. The authors would also like to thank M-H. Berger, M.Hiley and P.Sayers for electron microscopy work.

REFERENCES

1. *T.A.Edison U.K.Patent 4576 (1879).*
2. *J.W.Swan U.K.Patent 4933 (1880).*
3. *A.Shindo, R Fuji, M.Sengoku and Japanese Bureau of Industrial Technics Jap. Patent 4405 (1962).*
4. *A. Shindo "Graphite Fibre" Report of the Osaka Industrial Research Institute No. 317 (1961).*
5. *W. Johnson, L.N. Philips and W.Watt, U.K. Patent 1 110 791 (1969).*
6. *W.G.D.Carpenter, T.Lloyd, P.L. McMullan RAE Tech. Report 68519 (1968).*
7. *W.Watt W.Johnson RAE Tech Report 68288 (1968).*
8. *R.Moreton RAE Tech Report 69114 (1969).*
9. *W.Watt, W.Johnson CASI Transactions vol2, 2, (1969) 81.*
10. *W.Watt Carbon 10 (1972) 121.*
11. *S.Otani, Carbon , 3, (1965) 31.*
12. *S. Otani Carbon, 3, (1965) 213.*
13. *S. Otani, K.Yamada, T. Koitabashi and A. Yokoyama, Carbon, 4, (1966) 425.*
14. *M.A.A. Jorro, W.R. Ladner and T.D. Rantell, Carbon, 14, (1976) 219.*
15. *A.R.Postema, H.De Groot and A.J. Pennings, J.Mat Sci 25, (1990) 421.*
16. *D.J.Johnson, I. Tomizuka and O.Watanabe, Carbon 13, (1975) 321.*

17. G.G.Tibbetts, M.Endo and C.B.Beetz Jr, *SAMPE J.* 30, Sept/Oct (1986).
18. T.Koyama, M.Endo and Y.Onuma, *Jap J. Appl Phys* 11(1972) 445.
19. R.T.K. Baker and P.S. Harris, *Chemistry and Physics of Carbon*, Ed. P.A. Throver, 14, (1978), 83.
20. G.G. Tibbetts *Appl. Phys Lett* 42 (1983) 666.
21. G.G.Tibbetts *J.Crystal Growth* 73 (1985) 431.
22. H.T.Hahn and J.G.Williams, *Composite Materials: Testing and Design (Seventh Conference) ASTM STP 893*, J.M. Whitney, Ed., ASTM, Philadelphia, (1986) 115.
23. S.Kumar and T.E. Helminiak in "The Materials Science and Engineering of Rigid-Rod Polymers", W.W. Adams, R.K. Eby and D.E.Mclemore eds *Materials Research Society Symposium Proceedings vol. 134*, Pitts,PA (1989).
24. M.G.Dobb, D.J.Johnson, C.R. Park *J.Mat Sci* 25(1990) 829.
25. H.M.Hawthorne and E.Teghtsoonian, *J. Mat. Sci* 10 (1975)41-51.
26. D.J.Boll, R.M.Jensen, L.Cordner and W.D. Bascom *J.Comp. Mats.*, 24, (1990) 208.
27. J.M.Prandy and H.T.Hahn *SAMPE Q.* Jan 1991 p47-52.
28. S.Kumar, D.P.Anderson, A.S.Crasto *J.Mat. Sci* 28(1993) 423.
29. G.Niederstadt, *Z.Flugwiss. Weltraumforsch* 5 (1981) Heft 1, 30.
30. D.D. Edie, N.K.Fox, B.C.Barnett and C.C.Fain, *Carbon* 24 (1986) 477.
31. D.D.Edie, G.J. Hayes, H.E.Rast C.C.Fain *High Temperatures-High Pressures* 22 (1990) 289.
32. B.Rhee *High Temperatures- High Pressures* 22 (1990) 267.
33. H.B.Shim, J.I.Lee, H.S.Kim, Y.J.Cho, B.S.Rhee In *Proc of Advanced Composites '93 International Conference on Advanced Composite Materials* T.Chandra and A.K.Dhingra Eds, *The Minerals, Metals and Materials Society* (1993) 771.
34. . F.T. Gentile, M.J. Lysaght and N.F. Warner, *International Patent WO92/18224* (1992).
35. S.E. Moore Sr *U.S. Patent 5 320 512* (1994).

36. E.Fitzer European Patent 0 433 431 (1991).
37. E.Fitzer, W.Metzler, Carbon '92, Proc of the 5th International Carbon Conference, Essen, Germany June 22-26 (1992) 647.
38. International Committee for Characterisation and Terminology of Carbon First Publication of 30 Tentative Definitions Carbon 20 (1982) 443.
39. W.Watt, L.N.Philips and W.Johnson, The Engineer(London), 221 (1966) 815.
40. W.Watt and W.Johnson, Appl. Polym. Symp 9 (1969) 215.
41. A.J.Clarke and J.E. Bailey Nature 243 (1973) 146.
42. O.P.Bahl and L.Manocha, Carbon 13 (1975) 297.
43. T.-H.Ko, H.-Y. Ting and C.-H.Lin, J.Appl Polym Sci, 35 (1988) 631.
44. T.-H. Ko, P.Chiranairadul and C.-H. Lin Polym. Engineering and Sci., 31, 19 (1991) 1618.
45. S.J; Rosenblaum J. Appl Polym Sci 15 (1965) 2071.
46. G.K. Layden J.Appl Polym Sci 15 (1971) 1709.
47. J.-S. Tsai and H.-N Hsu J.Mat Sci Lett 11 (1992) 1403.
48. O.P Bahl and L.M Manocha Fibre Sci and Tech. 9 (1976).
49. T.Uchida, I Shinoyama, Y.Ito and K.Nukuda in Proc of 10th Biennial Conf. On Carbon, Bethlehem, Penn, USA (1971) 3150. J.-S. Tsai J.Mat Sci 11 (1992) 140.
50. J.-S. Tsai SAMPE Q. 24, 3, (Apr 1993) 21.
51. J.-S. Tsai, C.J.Wu and S. Chou, SAMPE J. 29 3, (May/June 1993) 23.
52. O.P Bahl and L.M Manocha Carbon 12 (1974) 417.
53. R.Moreton and W.Watt Carbon (1974) vol 12 543.
54. T.-H. Ko, S.-C. Lau, M.-F. Lin J.Mat Sci 27 (1992) 6071.
55. S.Kumar in Proc. of 35th International SAMPE Symposium 2nd-5th April 1990, Covina, CA (1990) 2224.
56. E.Tunistras and J.L. Koenig, J Chem Phys 53, 3(1970) 1126.

57. I.M. Robinson, M.Zakikhani, R.J. Day, R.J. Young and C.Galotis, *J.Mat Sci Letters*, 6 (1987)1212.
58. C.Galotis and D.N. Batchelder *J.Mat Sci Letts* 7, (1988) 545.
59. E.Fitzer, E.Gantner, F.Rosploch and D.Steinert, *High Temp. - High Pressure* 19, 5, (1987) 537.
60. F.Tuinstra and J.L.Koenig, *J.Comp Materials* 4, (1970) 492.
61. C.L.Angell and J.C. Lewis, *Carbon* 16 (1978) 431.
62. T.C. Chieu, M.S. Dresselhaus and M.Endo, *Physical Review B*, 26, 10 (1982) 5867.
63. C.H.Chang, R.A. Beyerlein and S.A.Chan, *Carbon* 22 (1984) 393.
64. A.Mizoguchi, Y.Yamaguchi, J.Shioya, Y.Ueba and H.Matsubaraa in *Proc and Program 18th Biennial Conf on Carbon*, Am Carbon Soc., Philadelphia, PA USA (1987) 358.
65. J.Heremans, I.Rahim and M.S. Dresselhaus *Phys. Rev. B* 32, 10 (1985) 97.
66. C.Galotis, N.Melanitis, D.N.Batchelder, I.M. Robinson and J.A. Peacock, *Proc of "Interfacial Phenomena in Composite Materials '89"*, Butterworths & Co. (1989) 97.
67. M. Guigon, *Ph.D. Thesis, Université de Technologie, Compiègne* (1985).
68. R.E.Palmer and S.W.G.Travis *Tech.Report DERA/MSS/MSS3/TR 9900001/1.0*.
69. R.Moreton and W.Watt, *Nature* 247 (1974) 360.
70. W.S.Williams, D.A.Steffens and R.Bacon, *J.Appl. Phys.* 41, 12(1970) 4893.
71. W.N.Reynolds and J.V.Sharp, *Carbon*, 12 (1974) 103.
72. J.B.Jones, J.B.Barr and R.E.Smith, *J.Mat Sci* 15(1980) 2455.
73. R.Moreton *RAE Tech. Report 77079* (1977).

<i>Temperature / °C</i>	<i>Aromatisation Index / %</i>
<i>Pilot plant</i>	33
<i>Bench scale</i>	
200	9
210	19
220	33
230	44
250	63

Table 1 Aromatisation Index (AI) calculated by Tsai's method [47,50-52] for different oxidation regimes.

Fibre	Intensity ratio (I_D/I_G)
T300	0.64 ± 0.01
Hollow carbon	0.65 ± 0.13

Table 2 Comparison of disorder ratio measured (using laser Raman spectroscopy) for T300 and hollow carbon fibre.

Fibre type	Diameter µm	Ultimate Tensile Strength GPa	Standard deviation GPa	Modulus in Tension GPa	Standard deviation GPa
T300*	7	3.53		235	
T300 tested	7 ± 0.9	3.21	0.74	242	61.1
DERA carbon fibre	6.38 ± 0.62	3.03	0.81	245.13	23.69
Preliminary hollow carbon	34.78 ± 2.7	0.38	0.09	106.52	16.67
Present hollow carbon	38.4 ± 2.4	0.52	0.2	249.4	120.5

*Manufacturer's data

Table 3 Comparison of tensile properties of preliminary hollow carbon fibre with solid carbon fibre.

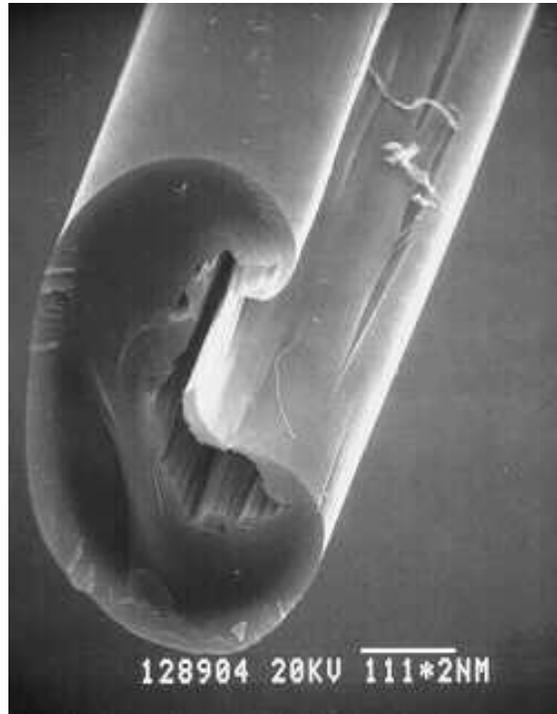


Figure 1 Hollow carbon fibre with an inconsistent wall thickness.

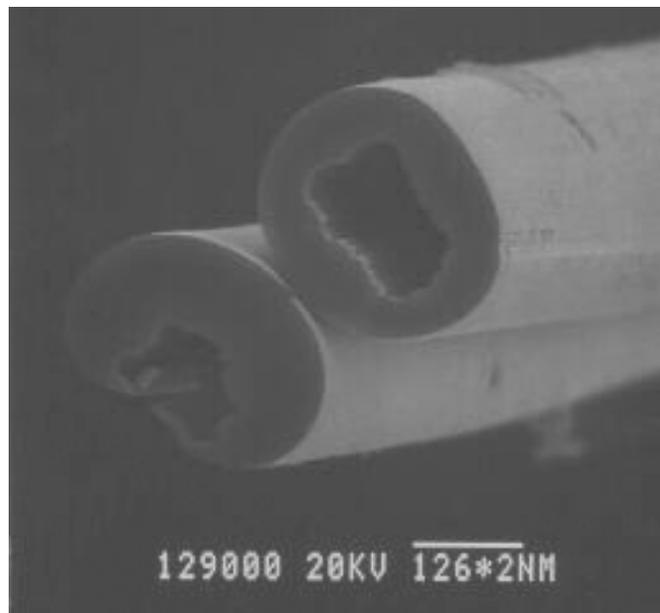


Figure 2 Hollow carbon fibres showing a central and non-centred lumen.

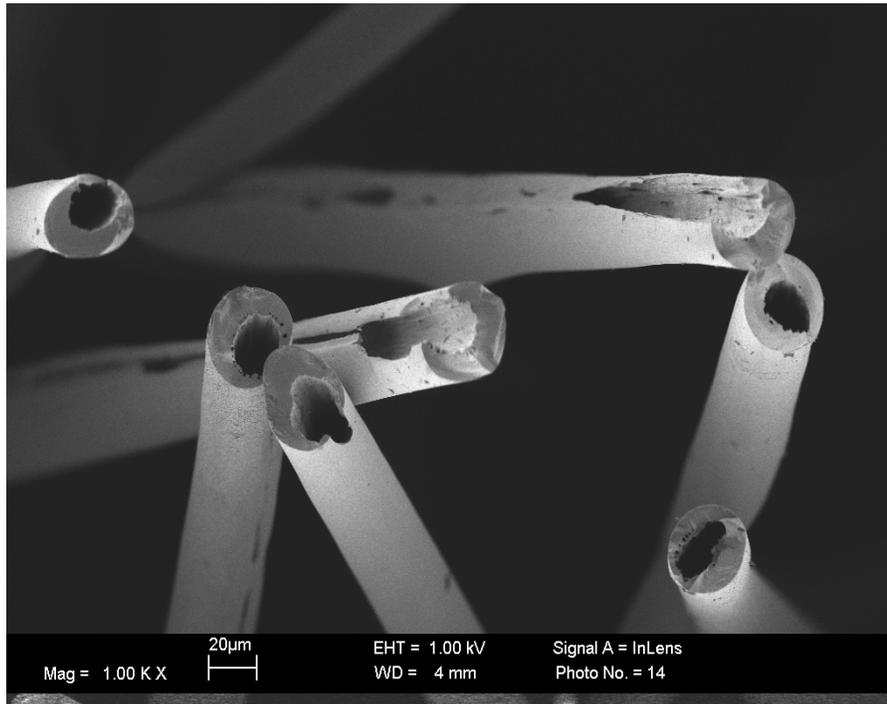


Figure 3 Hollow carbon fibres exhibiting a variety of cross-sectional profiles.

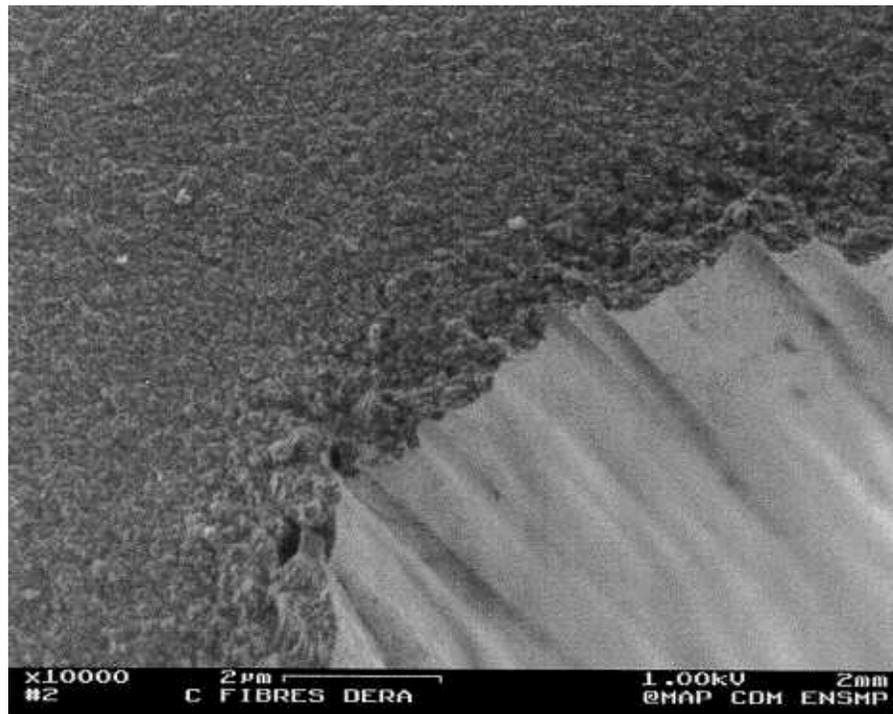


Figure 4 Detail of fracture surface of hollow carbon fibre. The granular appearance corresponds to typical high strength solid carbon fibre [24, 28, 54,55].

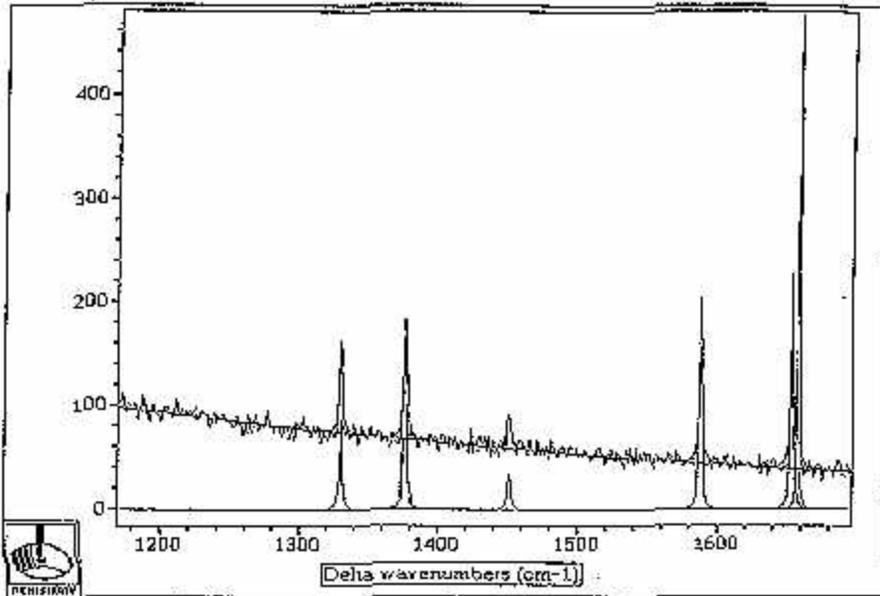


Figure 5(a) Raman spectrum for T300.

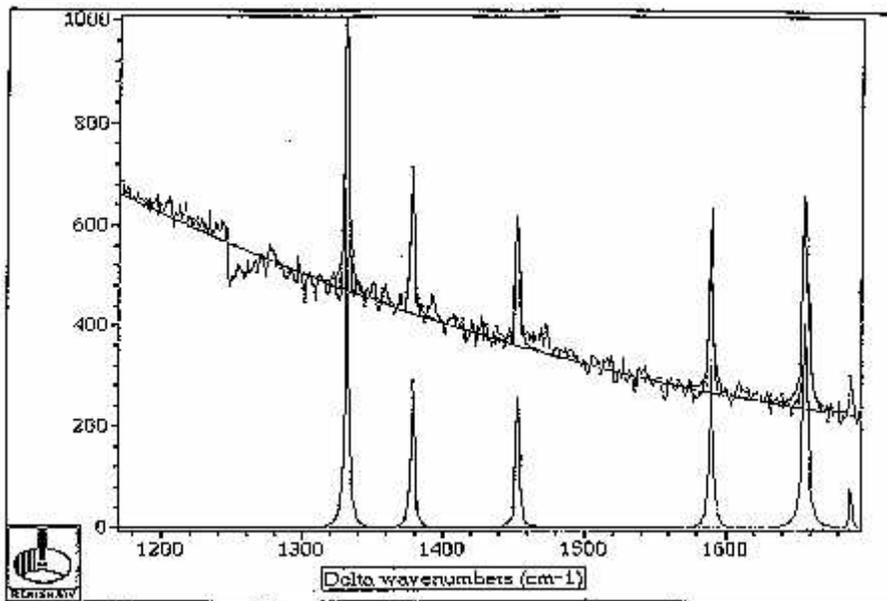


Figure 5(b) Raman spectrum for hollow carbon fibre.



Figure 6 C002 lattice fringe image showing a mean orientation of the aromatic layers parallel to the fibre axis (vertical) which is very similar to high strength carbon fibre.



Figure 7 C₀₀₂ lattice fringe image exhibiting a less oriented structure of the aromatic planes towards to the fibre axis (vertical).