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The development of composite carbon fibres of large diameter – macro fibres

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This paper describes the development of a process for manufacturing carbon fibres of larger diameter than those normally available from the "RAE process" [1] or other routes which have so far been described (e.g. the hot-stretching of pitch [2] or cellulose-based [3] fibres). The method consists of impregnating a bundle of carbon fibres or their precursors with resin and after curing, subjecting the composite fibre to a controlled carbonization. The end-product is a thin rod or fibre of carbon-fibre reinforced carbon, which can, in principle, have any desired cross-sectional shape or area [4].

Experiments have been conducted to discover the effect of various processing variables on the properties of the composite fibre. Having chosen a suitable resin for impregnation the principal variables are (a) the degrees of pyrolysis of the initial fibre before impregnation, (b) the rate of cure of the resin to form the "intermediate" and (c) the rate of temperature rise and the maximum temperature during the carbonization process.

Fibres of reasonable properties (Young's modulus 76.8 GN m^{-2} and ultimate tensile strength of 267 MN m^{-2}) have been produced but improvements should be obtainable by optimization of this basic process as fibres with strengths up to 400 MN m^{-2} have been observed.

1. Introduction

The diameter of the reinforcing fibre can influence some of the properties of a composite material, in particular its toughness and compressive strength. It has been suggested [5] that fibres with a diameter of 25 to 50 µm would be more satisfactory than those currently available which have a diameter in the range 5 to 10 µm. The most suitable diameter will depend on the properties required in the composite and the techniques used in fabrication [6].

Some advantages of thick fibres include:

(i) greater rigidity of individual fibres. This gives a greater ease in alignment and handling and can also increase the compressive strength when this is governed by fibre buckling [7, 8];

(ii) decreased ratio of surface area to volume. This will be important when the fibres are liable to react with the matrix or the atmosphere. Also a protective coating of a required thickness represents a smaller fraction of the total cross-sectional area of a large fibre than a small fibre;

(iii) improved toughness of the composite. The toughness of several classes of composites increases with increasing fibre size, without loss of other properties [4, 5, 9].

(iv) A further advantage of large-diameter fibres lies in their greater ease of infiltration by a liquid matrix either polymeric or metallic. This will be so regardless of surface tension effects because of reduced viscous drag.

Some disadvantages may, however, be encountered using large-diameter fibres. These typically arise because of the large minimum radius of curvature to which the fibre can be bent, giving rise to problems in the handling or in the fabrication of sharply curved shapes. This phenomenon can also give rise to abnormally low values of fracture energy in flexure [10].

The high quality carbon fibres which have so far been reported are based on polyacrylonitrile (PAN) [1], pitch [2] or cellulose-based fibres [3]. Problems of spinning, as well as the time required to accomplish diffusion controlled reactions

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(e.g. oxidation of PAN and pitch-based fibres) have limited the range of fibre sizes which can be produced to 5 to 10 μm. It seems unlikely at the present time that the fibre manufacturing processes mentioned above will be able to produce easily carbon fibres of substantially greater thickness than those developed so far. We have, therefore, conducted experiments to see if it is possible to make a strong, stiff carbon fibre by enclosing a bundle of carbon fibres or their precursor in a resin, and then carbonizing the composite fibre to produce a fibre of carbon-fibre reinforced carbon.

In this paper the following terms will be used.

Initial fibre: either a conventional carbon fibre or the oxidized PAN precursor fibre. The latter fibre may have been subjected to further heat-treatment in an argon atmosphere to temperatures between 200 and 1000° C.

Intermediate fibre: a bundle of initial fibres which has been impregnated with resin and then treated at temperatures near 200° C to cure the resin.

Macro fibre: an intermediate fibre which has been carbonized in an argon atmosphere at temperatures between 200 and 1300° C.

2. Apparatus

Three principal pieces of apparatus were used for the experiments.

2.1. The pre-treatment furnace

This was a horizontal tube furnace for the continuous pyrolysis of oxidized PAN (obtained from RAE Farnborough as a continuous 750 filament tow). The fibre entered and left the furnace through mercury seals to preserve the argon atmosphere in the furnace. The winding of the furnace was asymmetric to provide a slow, uniform rate of temperature rise and a rapid fall after the maximum temperature (up to 1000°C) was reached. The fibre was drawn through the furnace and wound onto a motor driven reel provided with a traversing mechanism.

2.2. Impregnation and cure apparatus

Reels of the initial fibre were then transferred to a second apparatus for impregnation with the resin. The fibre tow was passed through either a resin bath which was provided with a set of rollers (Fig. 1), or a bath in the form of a smoothly curving "u" of glass tube. On emerging from the bath, the excess resin was removed from the tow by passing it through a shaped die of either glass or silicone rubber. The glass dies were glass tubing drawn down to the required aperture, while rubber dies were prepared by casting around a similarly drawn glass rod.

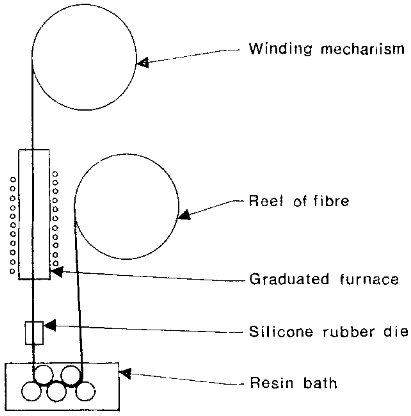

Figure 1 Schematic view of apparatus used for impregnation and curing of intermediate fibres.

2.3. Carbonization furnace

This was a platinum wound horizontal tube furnace (Stanton Redcroft Ltd) used with an argon atmosphere and provided with a programmed controller to give a constant temperature rise of between 0.25 and 10°C min^{-1}. Specimens were carbonized in this furnace using a variety of clamping devices which will be described later.

3. Choice of matrix resin

Thermogravimetric analyses (TGA) in inert atmospheres were made on several different possible matrix polymers including epoxides, phenolics and polyacrylonitrile. The primary requirement was for a resin material which would have as high a carbon yield as possible and which would not disintegrate during carbonization. The method of manufacture required a material which could be stored in the impregnation apparatus without solidifying, thus effectively limiting the choice to a polymer solution or to a "B-stage" resin with a long shelf life. The matrix finally selected was a partially polymerized phenolic resin, Aerophen 0807 (Messrs Ciba Ltd) which is an aqueous solution of approximately 50% solids content.

To evaluate the resin, blocks were cast and pyrolysed at temperatures up to 1400 in 100° C intervals. The volume shrinkage and weight loss

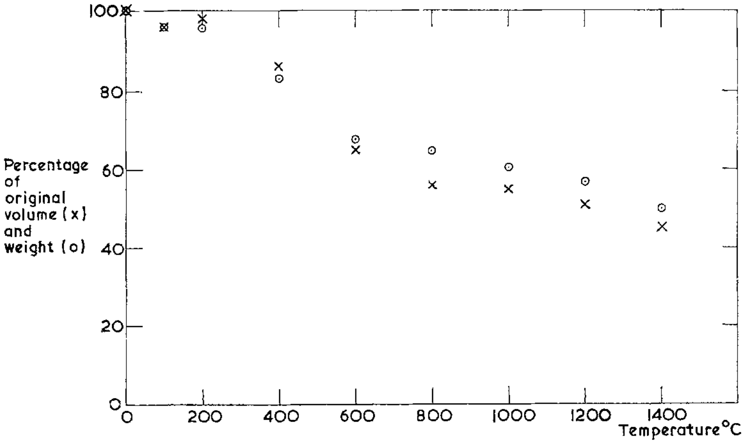

Figure 2 Volume shrinkage and weight loss of Aerophen 0807 as a function of temperature.

are shown in Fig. 2. The weight loss at 1000°C was 39.5%, leaving a carbon residue of 60.5%. Results obtained by TGA gave a slightly higher carbon residue of 67%.

4. Initial experiments

Originally it was thought that a satisfactory macro fibre could be made by impregnating a tow of type II carbon fibres with the resin, and then carbonizing slowly so that any differential contraction, especially of the matrix onto the fibres, could be accommodated by matrix creep during the process. Several trial filaments were produced by this method from normal carbon fibre tow, but although rates of pyrolysis as low as 0.5°C min^{-1} were used, the differential shrinkage caused severe cracking of the matrix and the interface was clearly very weak. Thus although satisfactory tensile properties could be obtained, the transverse strength of the fibre was always low. On bending such a fibre, a fibrous, brush-like fracture was obtained, accompanied by a cloud of carbon dust from the matrix. Matrix cracking could be eliminated by reducing the differential shrinkage between the fibres and the matrix. One possible method is to use a resin with a higher carbon yield. This method is unlikely to make a substantial improvement and an alternative method was devised.

Carbon fibres produced by the "RAE process" have their high strength and modulus inherent in their structure from the low temperature oxidization stage. However, during further heat-treatment stages shrinkage occurs of the same order as that given above for the matrix resin. Thus impregnating an oxidized or partially pyrolysed carbon fibre precursor tow and jointly pyrolysing fibre and resin allows a range of differential shrinkages (including zero difference) to be obtained [11]. It should be remembered that the primary carbon fibres in the macro fibres will only have, at best, properties appropriate to the pyrolysing temperature used for the macro

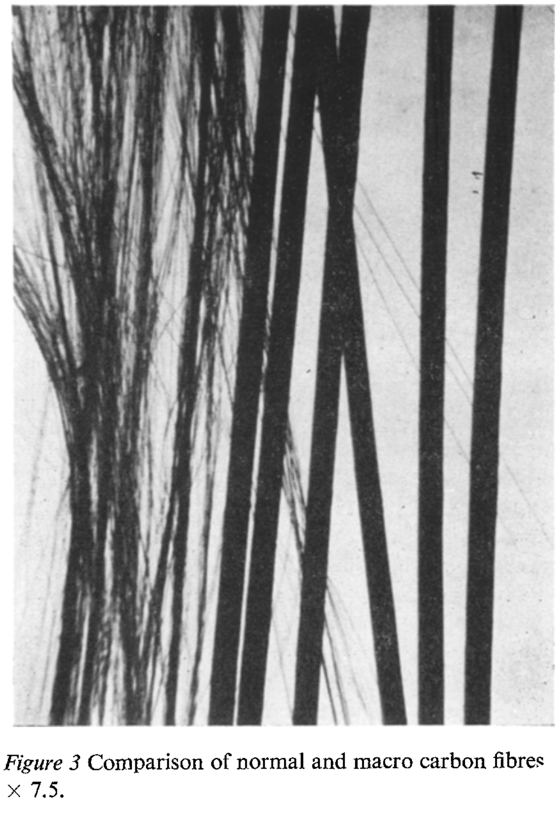

Figure 3 Comparison of normal and macro carbon fibres × 7.5.

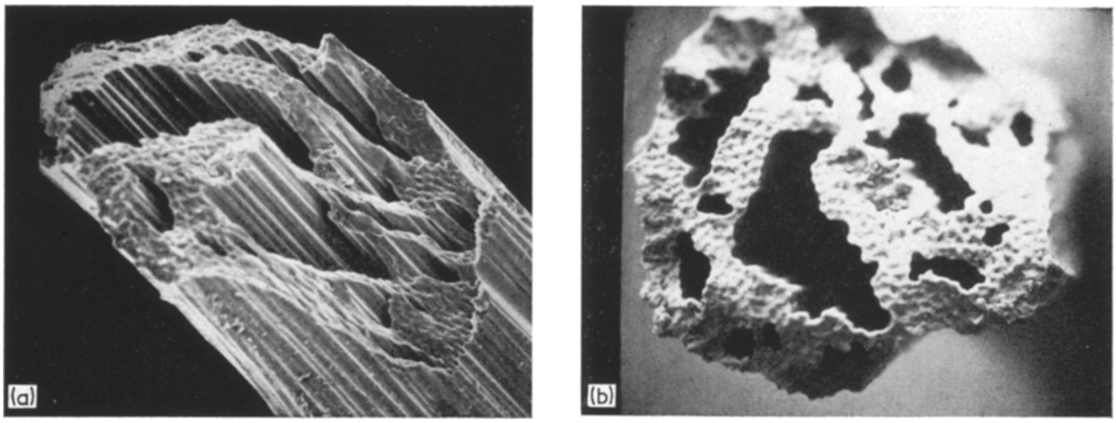

Figure 4 (a) Intermediate fibre (oxidized PAN/Aerophen 0807) passed through the curing furnace at 1.7 m h^{-1} (i.e. temperature rise rate of 9.3°C min^{-1} up to 200°C) × 100. (b) Same fibre as in (a), end-on view × 100.

fibre. A supply of continuous 750 filament oxidized polyacrylonitrile fibre was, therefore, obtained from RAE Farnborough, and was used in subsequent experiments.

Initial experiments showed that an excellent bond could be obtained between the oxidized PAN and the phenolic resin. It was also found that intermediates of this type could be pyrolysed to produce fully dense and crack-free macro fibres (Fig. 3). A series of experiments was then designed to find the optimum conditions for production of these fibres.

5. Production of the intermediate fibre

The quality of the intermediate fibre depends upon the impregnation and shaping process and upon the rate of curing of the matrix resin. Many experiments were made to improve the packing of the precursor fibres in the intermediate, and to improve its surface finish. Both properties are adversely affected by irregularities in the tow, and in particular by stray fibres which project from its surface. Great care must be exercised in handling the precursor tow, since it has been found that it is extremely difficult to apply corrective measures to disordered feedstock.

The intermediate fibres were examined in a scanning electron microscope (Stereoscan – Cambridge Instrument Co). Under some circumstances they were found to contain voids (Fig. 4a and b). It was established that the rate of curing the matrix resin had a direct influence upon the number of these voids, which were thus presumed to be due to the boiling off of water from the aqueous resin base, or from the condensation polymerization reaction. In no case, however, was it found possible to produce a completely void-free fibre, and this small residual porosity was attributed to the presence of small air-bubbles entrained in the fibre tow during impregnation. This conclusion was verified in a control experiment using an epoxy resin (Araldite MY-750 HY951; Messrs Ciba Ltd) which gave similar small residual porosities in spite of the fact that there are no volatiles produced in curing the resin. Nor are there any other volatiles present (e.g. solvents). The final rate of cure selected for producing the intermediate fibre was 1°C min^{-1}, which was found to give consistently good results.

6. Carbonization of the intermediate fibre

Following these experiments, batches of intermediate fibre were carbonized in an argon atmosphere in the furnace described above at temperatures between 200 and 1300°C. They were formed from untwisted 750 filament oxidized PAN impregnated with Aerophen 0807 and had been cured at a rate of 1°C min^{-1}. After heat-treatment, the fibres were removed and mounted for tensile testing. Two brass rods, provided with flats at one end, were held coaxially on a rigid support, and the fibres were glued across a 2 cm gap between the rods (Fig. 5). The rods projected beyond the support, so that the ends of the rods could be slipped into suitable pin grips on the testing machine (Instron Ltd). Before testing, the support was removed leaving the fibre attached at each end to a rod axially aligned in the testing machine.

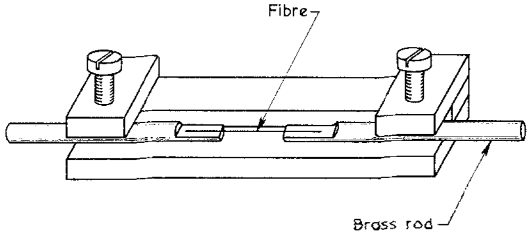

Figure 5 Jig for mounting single intermediate or macro fibres for tensile testing.

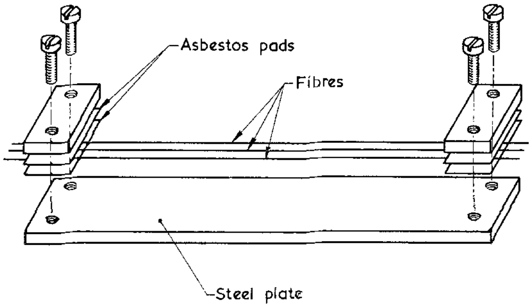

Figure 6 Original frame for pyrolysis of intermediate fibres.

6.1. Effect of final carbonization temperature

In the first group of experiments, to determine the effect of the final heat-treatment temperature, groups of four fibres were clamped between asbestos cloth pads on a mild steel frame (Fig. 6) and heat-treated at a rate of 0.5° C temperature rise per minute to temperatures in the range 200 to 1000° C. Heat-treatments to final temperatures in the range 1000 to 1300° C were made with the fibres clamped to a graphite frame using graphite clamps and screws. The fibres were maintained at the final temperature for 1 h.

The lateral shrinkage of the fibres is shown in Fig. 7 as a function of heat-treatment temperature. As expected, there was a progressive shrinkage as the temperature increased. The tensile strength (Fig. 8) first decreased slightly, then increased up to about 1000° C, and then decreased again. The Young's modulus (Fig. 9) showed a continuous increase up to about 1000° C, and then became erratic.

In general, the results obtained below 1000° C were as expected and do not call for comment. In the range 1000 to 1300° C, however, there was an unexpected drop in properties. This was presumed to be a consequence of the change at 1000° C from the steel to the carbon frame to which the fibres were clamped during heat-treatment. The steel clamping device was capable of exerting a much firmer hold on the fibres and prevented them from contracting during heat-treatment. Fibres which were loosely clamped (accidentally on the steel frame, or of necessity on the graphite frame) tended to be wavy along their length, difficult to mount, and weak. A further source of difference was the

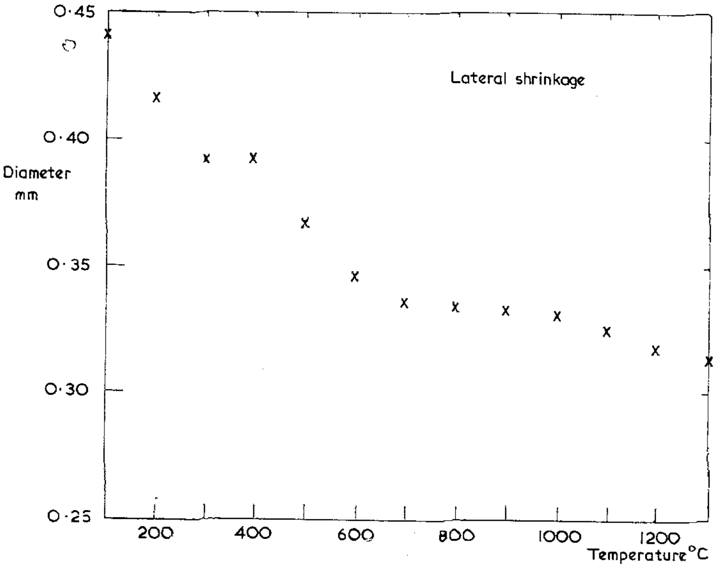

Figure 7 Lateral shrinkage of intermediate fibre as a function of pyrolysis temperature (initial fibre – oxidized PAN).

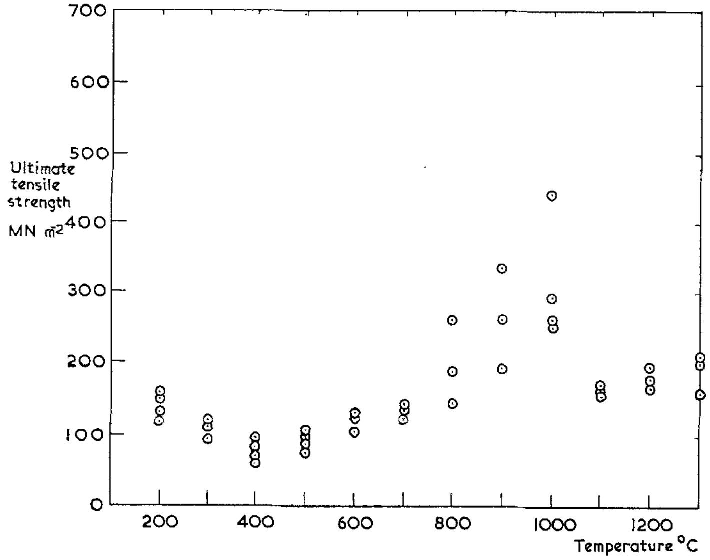

Figure 8 Strength of macro fibres for different pyrolysis temperatures (initial fibre – as for Fig. 7).

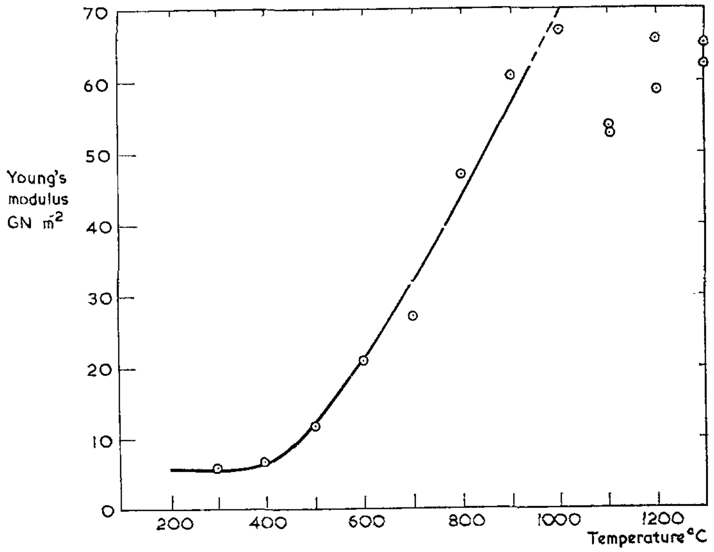

Figure 9 Young's modulus of macro fibres for different pyrolysis temperatures (initial fibre – as for Fig. 7).

different thermal expansions of the steel and graphite frames. As the expansion of the steel was greater, the fibres were given an uncertain additional stretch during heat-treatment on this device.

To overcome this problem and to provide a more constant tension during heat-treatment, another heating frame was constructed (Fig. 10). The fibres were fixed at each end between steel clamps which were placed out of the furnace hot zone. As before, asbestos cloth padding was used in the clamps and, in addition, a drop of phenolic

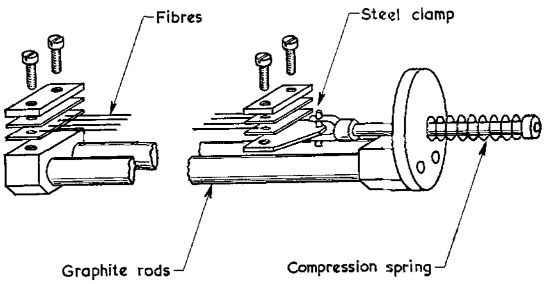

Figure 10 Modified frame for pyrolysis of intermediate fibres allowing shrinkage against spring tension.

resin was added as a further discouragement to movement. One clamp was fixed, while the other was allowed to move against a compression spring. This arrangement, using a relatively weak spring, allowed for differences in thermal expansion and for any shrinkage of the fibres during pyrolysis.

Intermediate fibres annealed to 1000° C on this frame were significantly stronger than those produced on the two previous frames. This is shown in Table I for fibres heat-treated to 1000° C.

TABLE I

Frame type	Mean fibre strength (MN m^{-2})
Clamped on graphite frame	170
Clamped on steel frame	176
Clamped in spring loaded frame	283

This last method of clamping was, therefore, adopted for use in all subsequent experiments.

6.2. Effect of varying the rate of carbonization

In the experiments described above, the rate of temperature rise during carbonization had been selected as 0.5° C min^{-1}, on the dual grounds that glassy carbon bodies are often made at similar heating rates, and that even lower rates would probably take an uneconomically long time. The selection of this temperature rate might have been unduly conservative, therefore a series of experiments was conducted to measure the strengths of macro fibres produced at different temperature rise rates in the range 0.25 to 10°C min^{-1}. Intermediate fibres prepared from oxidized PAN, as before, were heat-treated in the spring loaded frame at the rates shown in Fig. 11. The results show a clear trend, over most of the range: the slower the heating rate, the stronger the fibres.

There is some doubt, however, about the results obtained at a temperature rise rate of 0.25°C min^{-1}, as the fibres were weaker than those prepared at 0.5 and 1° C min^{-1}. The results have been checked and confirmed in a subsequent experiment. The effect is perhaps due to the time the fibre spends in the furnace (i.e. if there are traces of oxygen present, the fibres will be attacked and weakened – at a rate of 0.25°C min^{-1}, the fibres take over 50 h to reach 1000° C). In view of these results, it was decided that rates between 0.5 and 1 °C min^{-1} were the optimum for strength and time considerations, and all further work was performed within this range.

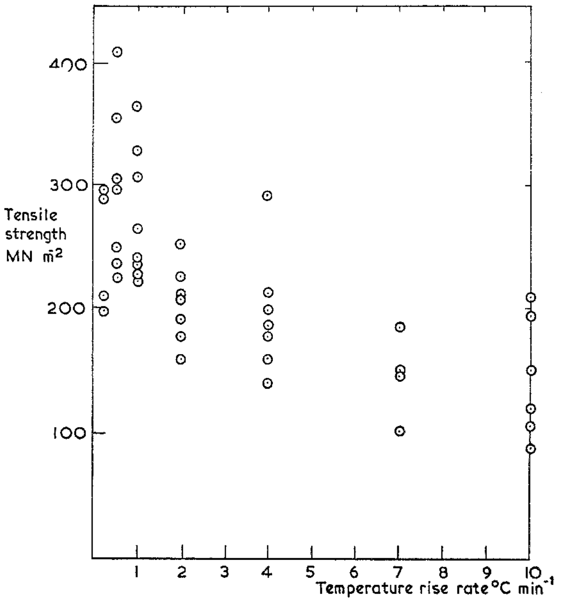

Figure 11 Tensile strength of macro fibres produced by pyrolysis to 1000° C at various rates of temperature rise.

6.3. Effect of pre-pyrolysing the oxidized PAN fibre

The earliest experiments reported above were conducted using type II carbon fibres as the initial fibre. After pyrolysis the macro fibres produced from the material were quite friable due to the large differential shrinkage between the initial fibres (0% shrinkage) and the resin matrix (~ 15% linear shrinkage) causing cracking of the matrix. On the other hand, the later macro fibres produced from oxidized PAN fibre had small relative shrinkage and good bonding between the fibre and matrix. These fibres were essentially pore- and crack-free. They had, however, been rather weaker than had been expected, in view of the volume fraction of primary carbon fibres (~ 50%) in the macro fibre. The best macro fibres had strengths of 355 MN m^{-2} (50000 lbf in^{-2}) which would imply (making a rough law of mixtures calculation) that the primary carbon fibres are carrying a stress of at most 710 MN m^{-2} (100000 lbf in^{-2}) at fracture. This seemed rather low even for carbon fibres that had only been heat-treated to 1000°C.

Stereoscan observations of the fracture surface of these macro fibres produced from an oxidized PAN fibre showed that cracks starting from surface flaws had been able to traverse the whole cross-section of the fibre, cutting primary fibres and matrix with apparently equal facility (see Fig. 12).

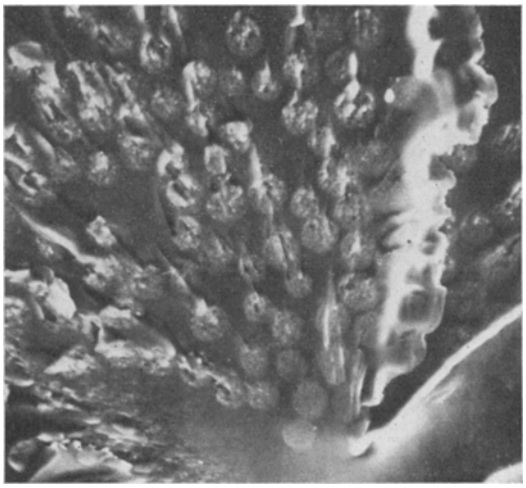

Figure 12 Fracture surface of macro fibre (intermediate fibre produced from oxidized PAN) showing brittle nature of material. Pyrolysed to 1000°C × 500.

Since it seemed unlikely that a completely flaw-free surface could be obtained, it was decided to attempt to alter the properties of the interface between the primary carbon fibres and the carbon matrix in such a way as to make the macro fibre less susceptible to rapid transverse crack propagation. It has already been recorded that macro fibres produced from type II carbon fibres were not susceptible to brittle-type fracture, but tended to split. Therefore, it was decided to see if it was possible to produce a strong macro fibre by adopting a compromise between the two extremes of oxidized PAN and type II carbon fibres. Accordingly, an experiment was performed in which intermediate fibres were prepared from oxidized PAN fibres which had been heat-treated at temperatures in the range 200 to 1000°C. In this way it was hoped to obtain a degree of differential shrinkage sufficient to discourage rapid crack propagation across the fibre while preserving a satisfactory transverse strength.

Accordingly, samples of oxidized PAN fibre containing 750 filaments were pyrolysed to temperatures of 200, 400, 600, 800 and 1000°C at a maximum rate of 0.5°C min^{-1}. These initial fibres were then made into intermediates by resin impregnation and were finally pyrolysed by heating to 1000°C at a rate of 1°C min^{-1} on the spring-loaded frame (Fig. 10). Tensile properties were measured for the initial fibres, the intermediates and for the final macro fibres. Mean values of ultimate strength and Young's modulus are shown in Table II for the different fibres. Three conclusions can be drawn immediately from this table. The first is that in terms of the properties of the macro fibre produced, there is little to choose between any of the initial fibres. Certainly there is no sign of any peak in tensile properties, which might have been expected in the compromise region between 200 and 1000°C. The second conclusion is that the intermediate fibres show the strength expected using a law of mixtures calculation based on the measured strengths of the precursor fibres. This indicates that there has been satisfactory impregnation of the intermediate fibre. Thirdly, there is a noticeable difference between the strength of the intermediate prepared from an oxidized fibre heat-treated to 800 and 1000°C and the properties which could be inferred from the strength of the macro fibre. Even if no allowance at all is made for the contribution of the carbon matrix, the strength values of the macro fibre are little more than half of the expected strength, while the Young's moduli are also low, but to a lesser degree.

A reasonable hypothesis to explain the discrepancy is to suggest that there had been some undesirable interaction between the precursor fibre and the matrix resin when carbonized together, which prevented the primary carbon fibres developing their full properties even when they had been partially carbonized before impregnation. This may be plausible for oxidized fibres heat-treated to less than 500°C, but it seems unlikely that an already carbonized fibre would be substantially altered.

It has been shown in Section 6.1 that warping of the macro fibres gives low strength values; this is a possible explanation. These problems will become more pronounced as the intermediate fibres are treated at higher and higher temperatures, by reason of the rapidly increasing stiffness of the fibre. It may well be that the method of tensile testing requires modification. Table II also shows the higher strength obtainable by heat-treating at 1200°C, which corresponds approximately to the temperature at

TABLE II

	Oxidized fibre treatment temperature (°C)				
	200	400	600	800	1000
Initial fibre properties					
Diameter (μm)	12.76	11.04	9.98	8.53	8.11
Ultimate strength (MN m^{-2})	206.6	257.6	377.6	440.4	1057.0
Young's modulus (GN m^{-2})	—	14.2	43.0	92.0	201.2
Intermediate fibre properties					
Diameter (mm)	0.485	0.403	0.385	0.398	0.320
Volume fraction of precursor fibre	53	56	50	34	48
Ultimate strength (MN m^{-2})	136.2	140.9	226.8	240.7	462.9
Young's modulus (GN m^{-2})	—	8.4	21.2	33.9	59.2
Macro fibre properties (after heating to 1000°C)					
Diameter (mm)	0.358	0.310	0.314	0.330	0.292
Ultimate strength (MN m^{-2})	266	251	221	136	267
Young's modulus (GN m^{-2})	56	70.9	66.9	54.3	76.8
Macro fibre properties (after heating to 1200°C)					
Diameter (mm)					0.285
Ultimate strength MN m^{-2}					370.0

which optimum strength properties are developed in normal PAN based fibres.

7. Conclusions

A method has been described whereby, in principle, carbon fibres of high strength and stiffness but of arbitrary cross-sectional area and shape may be made. This is done by impregnating a tow of carbon fibres (or their heat-treated precursor fibres) with a resin and pyrolysing the composite fibre so produced. Such large diameter fibres may be of value in the production of composites by virtue of their easier handling and infiltration by a liquid matrix and, because of their decreased surface area-to-volume ratio, their increased stability. They may also confer desirable properties, such as increased toughness and compressive strength on the finished article.

Several of the important process variables have been investigated. These include the selection of a suitable fibre and resin combination, the method for impregnating the tow with resin and the optimum rate of cure to produce a void-free intermediate. The pyrolysis of the intermediate has been followed and an optimum rate has been determined. The effect of partially pyrolysing the oxidized fibre has been studied in order to determine whether there is an optimum differential shrinkage between the initial fibres and the resin during the final pyrolysis.

These investigations have so far not shown how to produce a composite carbon fibre of outstanding properties. In particular, the question must be asked whether there is not some unexpected interaction between the primary fibres and the matrix which is limiting the properties of the primary fibres and, hence, of the composite fibre. On the other hand, most of the experiments have been limited to carbonizing temperatures of 1000°C, where normal PAN based fibres do not themselves have outstanding properties. Fibres have been produced with a Young's modulus of 76.8 GN m^{-2} and an ultimate tensile strength of 267 MN m^{-2} after heat-treatment at 1000°C. A few experiments at 1200°C suggest that superior properties are obtainable (see Table II), and further investigation of the fibre properties in the range of 1300°C upwards would appear desirable.

The joint pyrolysis of partially pyrolysed initial fibres and matrix has allowed the undesirable effects of matrix shrinkage to be overcome. It may now be possible to consider alternative polymeric matrix materials which have lower carbon residues, but which do not produce gaseous reaction products on curing. In this way, the low curing rates which must currently be employed with the phenolic matrix could perhaps be substantially increased.

Since this project was completed several papers [12-14] have been published describing the manufacture of carbon fibre/carbon articles. These papers, between them, discuss the choice of matrix resin, the increase in density obtained through re-impregnation or the use of fillers (e.g. graphite) and the effects of resin shrinkage during pyrolysis. It is interesting to note that in these papers a pressure-cured phenolic-based system was found to be the best matrix material, and that optimum properties were obtained by pyrolysing to 2600°C. In this project, a continuous system was chosen as providing the best production method and it would not be easy to use pressure curing.

Further work on large diameter carbon fibres could involve curing the phenolic resin under pressure, for example, pultrusion using a heated die may be a possible technique to obtain a pressure-cured continuous fabrication method. Also the use of alternative matrix materials and the effect of pyrolysing in the temperature range of 1300 to 3000°C could be considered.

Acknowledgements

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