Letters

Further Observations Concerning the Effect of Diameter on the Fracture Strength and Young's Modulus of Carbon and Graphite Fibres made from Polyacrylonitrile

In a recent publication [1] the author demonstrated the dependence of fracture strength and Young's modulus on fibre diameter for a graphite fibre made from a polyacrylonitrile (PAN) precursor. The final heat treatment temperature (HTT) used in the production of this fibre was about 2500°C so that the average values of fracture strength and Young's modulus were found to be ~ 2.0 GNm^{-2} and ~ 380 GNm^{-2} respectively. These values are based on the results of 40 microtensile tests performed in our laboratory using a gauge length of 1 cm, and they differ slightly from those reported in reference 1 because a correction has been applied to the diameter measurements previously used to calculate strength and modulus. The correction was made by comparison with calibrated tungsten wires, kindly supplied by Messrs. W. Watt and W. Johnson of the Royal Aircraft Establishment, Farnborough, England.

The reported relationship between strength, modulus and diameter was deduced to be a consequence of the "sheath" and "core" type structure of the fibres. It was also suggested that the final HTT of the fibres was an important factor in this respect [1]. It is the purpose of this communication to present additional evidence which confirms that the final heat treatment temperature is an important factor which determines the degree to which strength and modulus are affected by fibre diameter.

De Lamotte and Perry [2] have reported a similar diameter effect for "Grafil HT" fibres. To the best of the author's knowledge this type of fibre is produced by the heat treatment of a PAN precursor to approximately 1500°C. According to the manufacturers (Courtaulds Ltd) this treatment yields a fibre with an average tensile strength of ~ 2.4 GNm^{-2} and a Young's modulus of ~ 260 GNm^{-2}. These values are obtained by tensile tests performed on a 5 cm fibre gauge length and, since the fracture strength is dependent upon gauge length, a correction must be applied in order to compare the manufacturers values for "Grafil HT" fibres with our values based on tests using a 1 cm gauge length. This is possible using the results of Moreton [3] who has studied the gauge length effect, and the normalised fracture strength for a fibre heat treated to 1500°C is computed to be ~ 3.0 GNm^{-2}.

It was suggested in reference 1 that the dependence of strength and modulus on diameter was not obvious in the case of fibres made from PAN which were heat treated in the range 1000 to 1200°C. This observation was based on the results of Shindo [4] and some preliminary studies performed at this laboratory. The fibres examined here were manufactured by Rolls Royce Ltd. Our tests, again using a 1 cm gauge length, indicate that this material has an average tensile strength of ~ 2.8 GNm^{-2} and a Young's modulus of ~ 215 GNm^{-2}. A total of 80 fibres have been tested and analysis has now revealed some evidence of a small diameter effect.

The relationship between fibre strength or modulus and diameter can be illustrated in linear terms using the method of least squares to obtain the best fit for the data [1, 2]. The correlations obtained are not good due to random variations in fibre structure, but they do serve to illustrate the extent of the diameter effect. Figs. 1a and b show the lines obtained by least squares fitting and the associated correlation coefficients (r) for a linear relationship of Young's modulus and fracture strength against fibre diameter for the three types of fibre discussed above. The results for the 1500°C fibre ("Grafil HT") are taken from de Lamotte and Perry [2], who used a test gauge length of 5 cm. Since the results reported for the 1000 to 1200°C fibre and for the 2500°C fibre are based on tensile tests using a gauge length of 1 cm, the fracture strength of these fibres appear artificially high compared to the data for the 1500°C fibre as shown in fig. 1b. The gradients of the lines shown in fig. 1, expressed in GNm^{-2} per micron diameter are compared in table I. Clearly the influence of fibre diameter on both fracture strength and Young's modulus becomes greater as the final HTT of the fibres is increased.

This observation is in accordance with the theory proposed in reference 1 to explain the

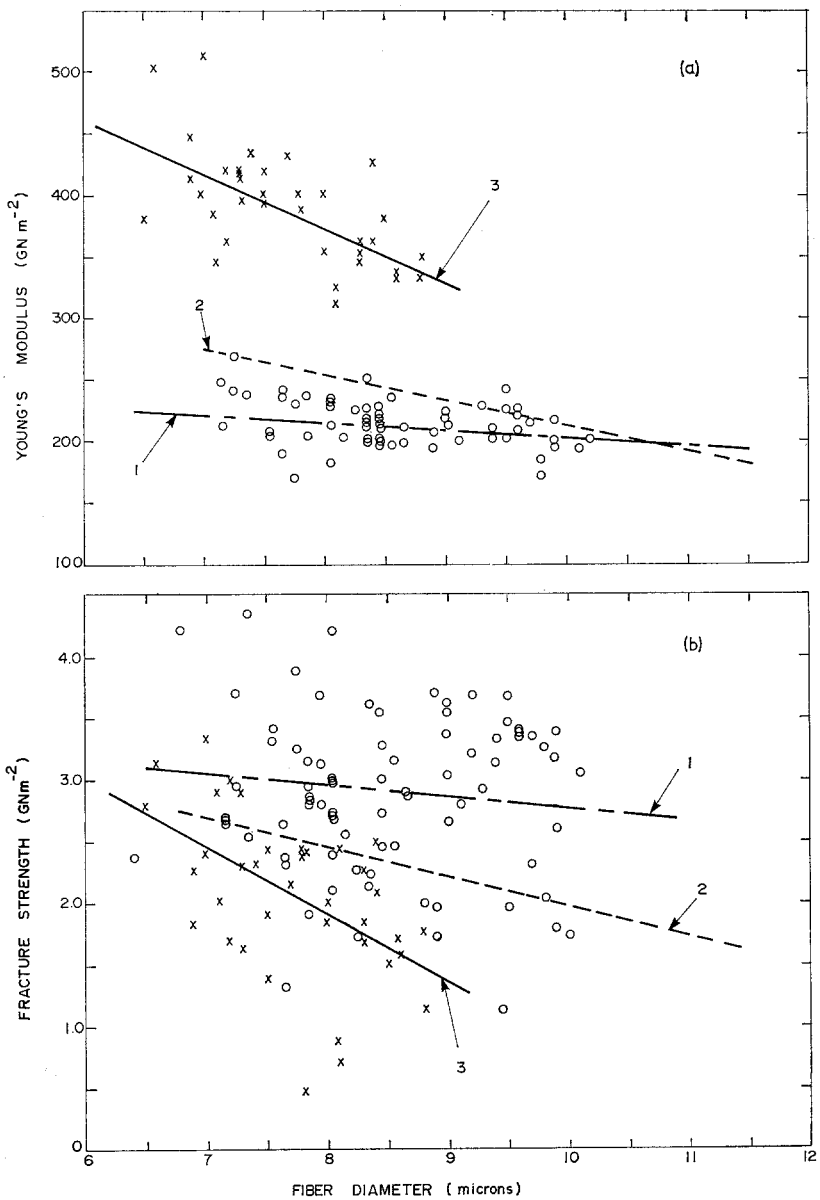

Figure 1 Comparison of the linear relationship between (a) Young's modulus and fibre diameter, and (b) Fracture strength and fibre diameter.
Line 1 — - - - - least squares fit for the 1000 to 1200 °C fibre
○ experimental points for the 1000 to 1200 °C fibre
Line 2 -------- least squares fit for the 1500 °C fibre (from reference 2)
Line 3 ———— least squares fit for the 2500 °C fibre
× experimental points for the 2500 °C fibre

diameter effect in graphite fibres. It was suggested that the two important factors which influence the diameter effect are (*a*) the extent of the preoxidation treatment given to the fibres at 220°C, and (*b*) the final HTT imparted to the fibres. The preoxidation treatment modifies the structure of the PAN precursor in such a way as to influence the alignment of the turbostratic

TABLE I Comparison of the gradients of the linear least squares fits for fracture strength and Young's modulus against fibre diameter for fibres heat treated to 1000 to 1200 °C, 1500 °C and 2500 °C

Final heat treatment temperature of fibres, ° C	Gradient of fracture strength versus fibre diameter $GNm^{-2}/\mu m$	Gradient of Young's modulus versus fibre diameter $GNm^{-2}/\mu m$
1000 to 1200	0.09	7.6
1500	0.29*	21.0*
2500	0.55	45.0

*Values calculated from reference 2.

graphite crystallites which form on subsequent heat treatment [5]. In most commercially available PAN precursor fibres, the preoxidation treatment is discontinued before complete oxidation of the precursor is achieved so that a "core" of unoxidised, unstabilised PAN remains. This results, after further heat treatment, in a duplex fibre structure with an outer "sheath" of well aligned crystallites and an inner "core" of less well aligned crystallites. As the final HTT is increased the alignment of the basal planes of the crystallites parallel to the fibre axis also increases. Thus, since the Young's modulus of the fibre is extremely dependent on the orientation of the crystallites, the "sheath" will have a higher Young's modulus than the "core". The diameter effect can then be explained in terms of the "law of mixtures" since the proportion of "core" in the thick fibres will be greater than in thin fibres. Increasing the final HTT will accentuate the difference between the Young's moduli of the "sheath" and "core" structures so that the increasing dependence of Young's modulus on fibre diameter is to be expected.

The dependence of fracture strength on fibre diameter can also be explained in terms of the sheath/core structure. On cooling from the final HTT, flaws will be formed due to internal stresses resulting from the differential thermal contraction in adjacent crystallites. The number of flaws formed will be greater in the less well aligned "core" region, but will also increase with the higher HTT due to increased internal stresses. In addition, because of the improvement in structure of the "sheath" with higher HTT, fewer flaws would be expected in this region of the fibre and hence the *difference* in the number of flaws occurring in the "sheath" and "core" will increase with HTT. The dependence of fracture strength, which is related to the flaws present, on fibre diameter is therefore expected to increase with increasing HTT.

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The Microstructure of Plasma-Anodised Alumina Films

Plasma anodising has been used by several workers [1-10] as a means of growing oxide layers on metals and semiconductors, and it is now finding application in the manufacture of electronic devices [11]. Surprisingly little attention has been paid to the microstructural aspects of the resulting oxide, and the purpose of this letter is to point out the potentialities of scanning electron microscopy for revealing the microstructure, and to indicate an important problem which can be studied by this means.

A piece of aluminium sheet 10 mm square by 1 mm thick was polished mechanically to produce a flat surface, and then polished electrolytically in a perchloric-acetic acid mixture to remove the cold-worked layer. Part of the surface was masked with lacquer, so as to provide a reference surface without an anodised film. The specimen was then transferred to a conventional vacuum-evaporator pumped by a liquid-nitrogen-trapped oil diffusion pump. After