The Effect of Fibre Diameter on the Mechanical Properties of Graphite Fibres Manufactured from Polyacrylonitrile and Rayon

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A relationship between diameter and both Young's modulus and tensile strength of graphite fibres, manufactured from both polyacrylonitrile and rayon precursors is demonstrated. Thin fibres exhibit higher values of Young's modulus and tensile strength than thick fibres. The observed relationship is deduced to be a consequence of the "sheath" and "core" type structure which is characteristic of these fibres.

1. Introduction

The scatter in experimental values for the Young's modulus and tensile strength of high modulus, high strength graphite fibres is explained in terms of the random variation of the fibre structure and the presence of flaws [1-3]. We have studied the tensile properties of a polyacrylonitrile (PAN) precursor graphite fibre and of commercial Thornel 50 graphite fibre and have discovered a consistent variation of both Young's modulus and tensile strength with fibre diameter. These results, therefore, indicate another factor which contributes to the variation in mechanical properties reported for these fibres and also provides some interesting evidence concerning their structure.

2. Experimental

The PAN precursor fibres, manufactured by the process of Watt, Phillips, and Johnson [4], were obtained from a private source. These fibres exhibited a tensile strength of ~ 1.7 GNm^{-2} (250000 lb. in.$^{-2}$) and a Young's modulus of ~ 345 GNm^{-2} (50×10^6 lb. in.$^{-2}$), properties typical of fibres heated to a graphitising temperature of $\sim 2500°$C. Their diameters, measured by optical microscopy, were generally in the range 6 to 10 μm. A few fibres had diameters larger than 10 μm, but these have not been considered in the present study.

The Thornel 50 fibres were purchased from Union Carbide and the manufacturer lists their tensile strength as 2.1 GNm^{-2} (304000 lb.in.$^{-2}$) and their Young's modulus as 363 GNm^{-2} (52.6×10^6 lb. in.$^{-2}$). The cross-section of these fibres is characteristic of the crenulated shape of the rayon precursor, so that cross-sectional areas are difficult to measure. However, for the purpose of this study it was considered adequate to measure the width of the fibres at several points along the test gauge length in order to obtain an "apparent" diameter. Such an approach is valid if a positive linear relationship exists between the measured "apparent" diameter and the true "equivalent" diameter of these fibres.

In order to check the validity of using the measured fibre width in calculating the strengths and moduli of Thornel 50S fibres, a simple experiment was performed to relate the "apparent" diameter to the true "equivalent" diameter of these fibres. A group of fibres was mounted, sectioned and photographs of the fibre ends were taken at a magnification of 1500×. A photograph was taken at the same magnification of a standard grid of known area. The cross-sectional area of each fibre was then measured by weighing, using the photograph of the standard grid as a calibration, and the value of true "equilvalent" diameter calculated. The maximum and minimum width of each fibre was then measured and plotted against the corresponding "equivalent" diameter of that fibre. The results are shown in fig. 1, and it is evident that the relationship between measured width and fibre diameter is reasonably linear. It is clear, however, that the "apparent" diameter measurements used in this work result in artificially large values for the cross-sectional areas of the Thornel fibres, so that the reported values for Young's modulus and tensile strength are correspondingly low. It is stressed, therefore, that the results presented for the Thornel fibre are intended to illustrate a trend and that the actual values of strength and modulus reported are of little significance.

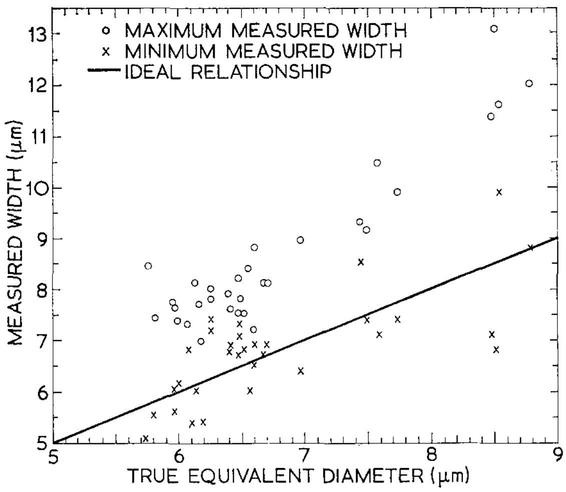

Figure 1 Relationship between "measured width" and the "true equivalent diameter" for Thornel 50 graphite fibres.

Both types of fibre were tested in a Tecam micro-tensile testing machine which has been adequately described by Marsh [5]. Single fibres of gauge length 1 cm were pulled to failure and values for Young's modulus and tensile strength were calculated using fibre diameter measurements obtained in the manner described above.

3. Results

Values of Young's modulus and tensile strength are plotted against fibre diameter for both types of fibre in figs. 2 and 3. The straight lines drawn on the graphs represent a first order fit between Young's modulus and diameter and tensile strength and diameter respectively. They were computed by the method of least squares and are included to illustrate the trend of the results rather than to indicate a first order relationship between the parameters. However, in all cases the general trend, that fibre strength and modulus decreases as fibre diameter increases, is clearly evident.

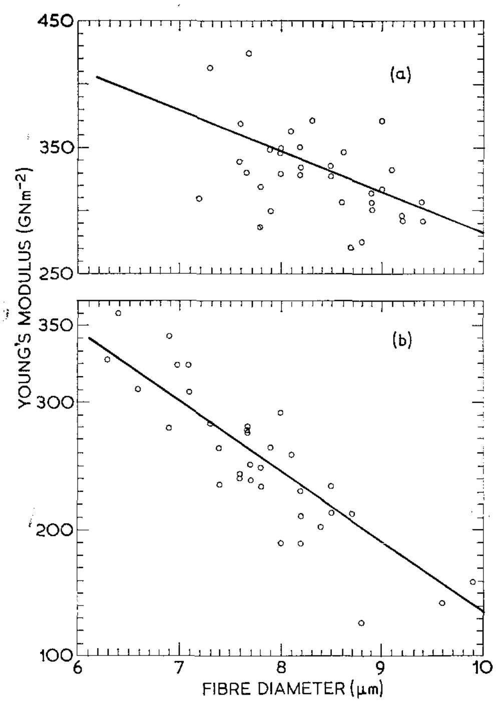

Figure 2 Effect of fibre diameter on Young's modulus of (a) PAN precursor graphite fibre. (b) Thornel 50 graphite fibre.

4. Discussion

4.1. General

Hitherto, no results indicating a relationship between fibre diameter and Young's modulus and tensile strength for high strength, high modulus graphite fibres made from PAN or rayon have been published. However, Shindo [6], who produced weaker fibres of low modulus from a PAN precursor, did indicate a similar relationship between fibre diameter and tensile strength. More recently Kawamura and Jenkins [7] noted a relationship between strength, modulus and diameter for their glassy carbon fibres made from phenol-hexamine polymers.

4.2. Modulus-Diameter Relationship

It has been shown [8-10] that the Young's modulus of both PAN and rayon precursor graphite fibres is controlled by the degree of orientation of graphite basal planes parallel to the fibre axis.

In order to explain the observed effect of

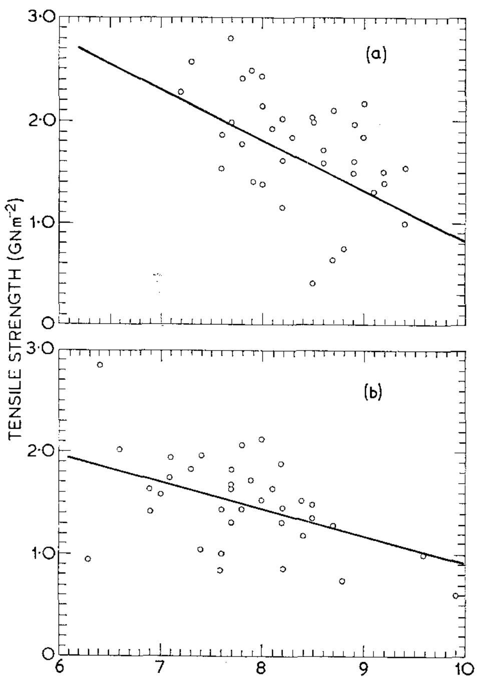

Figure 3 Effect of fibre diameter on the tensile strength of (a) PAN precursor graphite fibre. (b) Thornel 50 graphite fibre.

diameter on Young's modulus, it is necessary to consider the results of Butler and Diefendorf [11, 12] who demonstrated a difference in structure between the surface layers of the fibres and their interior. Crystallites close to the surface of the fibres tend to be larger and better aligned, parallel to the fibre axis, than are crystallites in the middle of the fibres. This "sheath" and "core" effect is illustrated in fig. 4.

Watt and Johnson [13] have recently discussed a "sheath" and "core" effect in PAN based fibres which is apparently influenced by the rate

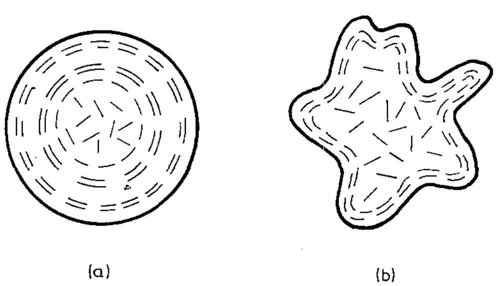

Figure 4 Schematic representation of basal plane alignment in (a) PAN precursor graphite fibre. (b) Thornel graphite fibre.

of diffusion of oxygen in PAN. It has also been suggested [12] that the "cores" of the graphite fibres result from the pyrolysis of unstabilised or partially stabilised polymer, whilst the "sheath" represents the structure derived from fully stabilised polymer. This suggests that the "sheath" and "core" effect is a result of the essential oxidation treatment of the precursor. Consequently, it is likely that the thickness of the sheath of well aligned crystallites is related to the diffusion rate of oxygen in the precursor fibre and is therefore independent of fibre thickness.

It is evident, therefore, that a greater fraction of a thin fibre will be composed of a "sheath" derived from "oxidised" polymer, whilst a thick fibre will contain a larger fraction of "core". Since, in the outer sheath, the crystallites align more consistently with their basal planes along the fibre axis, thin fibres should exhibit a higher modulus than thick fibres by virtue of their greater anisotropy. Support for this theory is found in the results of Watt and Johnson [13] who have shown that longer oxidation treatments, which increase the thickness of the sheath result in a higher modulus value in the fully graphitised fibre.

4.3. Factors Affecting the Tensile Strength of Graphite Fibres

It is well known that the tensile strength of carbon and graphite fibres is greatly influenced by the presence of flaws [1-3]. This is demonstrated by the dependence of measured strength upon the test gauge length. A positive relationship between fibre strength and Young's modulus exists for graphite fibres produced by pyrolysis of acrylic precursors at temperatures of up to about 1000° C [14]. However, as the heat treatment temperature is raised above about 1200 to 1500° C, the tensile strength decreases, while the Young's modulus continues to increase [1, 3]. This leads to the conclusion that the tensile strength of graphite fibre is relatively independent of Young's modulus and is strongly dependent on the presence of flaws.

It has been suggested [15] that the decrease in strength of PAN fibres with increasing temperature is a consequence of the breaking of cross-link bonds between crystallites. It is not obvious however, that such an occurrence will result in a simultaneous increase in modulus and decrease in strength when the fibres are heated above 1500°C.

The observed changes in modulus and strength can be explained, however, if it is accepted that high heat treatment temperatures can cause a specific type of flaw in the fibres. This flaw is visualised as a basal plane crack, formed during cooling in a similar manner to which Mrozowski cracks occur in bulk graphites [16]. Angular and shear stresses are induced in carbon and graphite structures through the anisotropic thermal contraction of the crystallites and this results in cracking, particularly at the points between crystallites. The occurrence of such cracks in bulk graphites has a significant effect in reducing their strength. The great strength of fibres compared to bulk graphite is probably because the induced stresses are minimised and fewer cracks occur, due to the homogeneity of the fibres and the regular alignment of crystallites. Also the cracks which are formed will tend to align close to the fibre axis so that they have a relatively small effect as stress raisers when the fibres are tested in tension along the fibre axis.

While it would require an extremely large number of such cracks to significantly affect the tensile Young's modulus by the elastic opening of cracks, only one crack, significantly misaligned relative to the fibre axis, is sufficient to affect the fracture strength of the fibre. Thus the above mechanism will result in a simultaneous increase in Young's modulus and decrease in tensile strength as the final heat treatment temperature is raised.

4.4. Tensile Strength – Diameter Relationship

Since the tensile strength of the fibres is influenced by the presence of flaws it is immediately evident that the variation in strength with fibre diameter might be explained as a simple volume effect, i.e. more flaws would be expected in a unit length of a thick, compared to a thin, fibre. However, in the case of PAN precursor fibres, there is sufficient information available to indicate that the simple volume effect does not account for the observed variation in strength with fibre diameter. The results shown in fig. 3 indicate that the strength difference between PAN fibres of diameter 6 μm and 10 μm is of the order of 1.7 GNm^{-2} (250000 lb. in.$^{-2}$). Since the specimens tested had a gauge length of 1 cm, the total volume difference between such fibres is $16\pi \times 10^{-8}$ cm^3. An equivalent volume difference exists between two fibres of 8 μm diameter (approximately the average diameter of this type of fibre) with gauge lengths of 0.5 cm and 1.5 cm respectively, yet according to Moreton [17] the difference in strength between two such fibres is only about 0.2 GNm^{-2} (30000 lb. in.$^{-2}$).

Studies made in our laboratory show that no relationship exists between diameter and strength for PAN based carbon fibres (heat treated to only $\sim 1200°$ C). The results of Shindo [6] support this observation. The fact that the strength-diameter relationship appears as the fibres are heated to higher temperatures suggests there may be a relationship between this effect and the occurrence of Mrozowski cracks.

Since basal plane cracks occur as the results of the anisotropic thermal contraction of the crystallites, more cracks will occur in a structure where the crystallites are randomly oriented. In thick fibres the "core", where crystallites are less well aligned than in the "sheath", constitutes a larger fraction of the volume than in thin fibres. Thus more cracks are likely to occur in a thick fibre than in a thin one. Superimposed upon this factor is the effect of crack orientation relative to the tensile or fibre axis. Misorientation of basal planes is greater in the "core" than in the sheath and hence there will be a greater number of cracks in a thicker fibre which are oriented at a significant angle to the fibre axis. A crack which is at a large angle to the fibre axis will, of course, be more effective as a flaw than a crack of equivalent size aligned close to the fibre axis. Thus thick fibres will contain more basal plane cracks, and these cracks will probably be oriented at a significant angle to the fibre axis. It follows therefore that the thicker fibres will exhibit lower tensile strengths compared to thin fibres.

5. Conclusions

The Young's modulus and tensile strength of graphite fibres made from PAN and rayon precursors are significantly affected by fibre diameter in the range 5 to 10 μm. Thinner fibres exhibit both a higher strength and a higher modulus than do thicker fibres.

The observed variation in Young's modulus has been explained by differences in the relative amounts of "sheath" and "core" in fibres of different diameter.

It is suggested that the tensile strength of graphitised fibres is influenced by the presence of basal plane cracks which result from the anisotropic thermal contraction of the crystallites. The number of cracks which are likely to occur and their severity as flaws is again related to the "sheath" and "core" type structure and explains the observed variation in tensile strength with fibre diameter.

The occurrence of basal plane cracks can also explain the inverse relationship between strength and modulus for fibres heated above ~ 1500° C.

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