The fracture mechanism of carbon fibres

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The physical properties of carbon fibres have been related to their structure by considering the influence of ribbon unbending during extension. An explanation of the fibres' anomalous strength characteristics, based on their structure and not on the presence of internal flaws, is presented.

1. Introduction

Carbon fibres are currently the subject of considerable interest because their high strength and modulus, coupled with low density, makes them ideal materials for use in fibrous composites. Of particular interest has been the decrease in strength which accompanies increasing modulus as the heat-treatment temperature of circular fibres derived from polyacrylonitrile (PAN) [1] is increased. One would generally have expected the strength of a material to increase with modulus. The anomalous behaviour of carbon fibres is thought to be due to the presence of flaws [2-5] and the observation that the fibre strength increases with decreasing sample length has been taken as confirmation of this view [5].

Surface flaws have been clearly implicated as the major source of fracture in fibres heated to low temperatures [2] (below 1200°C) but, for higher heat-treatment temperatures, surface flaws do not appear to greatly influence the strength of the fibre [2] and so the "flaws" which initiate fracture have been supposed to lie in the interior of these fibres [2-4]. A number of different types of flaw, such as inclusions [3], voids [4] and small areas of 3-D graphite [6], have been implicated, but, in general, these seem to be insufficiently abundant to offer a completely adequate explanation for fibre fracture. It is the purpose of this paper to question the fundamental hypothesis that fracture in carbon fibres treated at temperatures above 1200°C is initiated by flaws or imperfections in the fibre and to indicate that the fracture behaviour of carbon fibres is explicable in terms of their fine structure alone.

2. Fibre structure

On the basis of electron microscopy and X-ray diffraction studies, the structure of carbon fibres has been established as a number of intermittently connected undulating ribbons aligned roughly parallel to the fibre axis and separated over the greater part of their length by extended microvoids of the order of 1 nm in diameter [7, 8]. These ribbons tend to be straight over portions of their length and curved over the remainder [7]. The ribbons are stacks of graphite layers in tubostratic array [7] and, depending on the heat-treatment temperature to which the fibre has been subjected, have average transverse dimensions between 1 and 10 nm [9, 10].

An attempt to relate the mechanical properties of carbon fibres to their structure has envisaged an elastic unwrinkling of these ribbons [7, 11], but the forces involved in the unbending implicit in this concept have not received adequate consideration. Because each ribbon is surrounded over most of its length by microvoids, considerable independent ribbon movement is possible and so the forces involved in ribbon unbending must influence the tensile properties of the fibre. Of particular interest in this context is the high stress produced by tensile loading in the concave edge of curved members [12] and it is proposed that this feature offers an explanation for the anomalous loss in strength observed when the modulus of carbon fibres is increased.

3. Structure model

A simplified mechanical analysis of one of these undulating ribbons may be made on the basis of the model illustrated in Fig. 1.

This model envisages a ribbon of thickness h

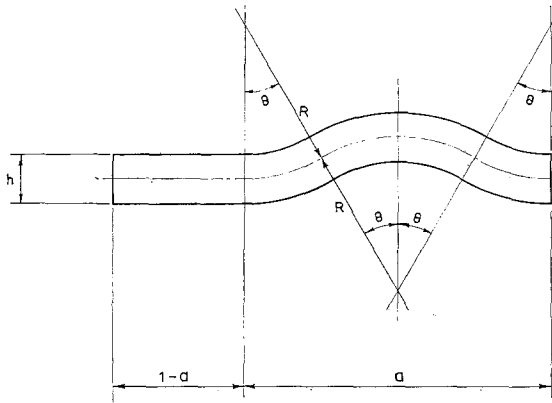*Present address: Medical Research Council, Laboratory of Molecular Biology, Cambridge, CB2 2QH.

Figure 1 Simplified structure model on which the mechanical analysis is based.

$$\epsilon_b = \frac{\sigma R^2}{E_t h^2 \sin\theta} \ [\theta(18 + 24\cos^2\theta - 24\cos\theta) - 9\sin 2\theta]$$

$$\epsilon_t = \frac{\sigma}{E_t \sin\theta} \ [5/4 \ \sin2\theta + \theta/2] \ .$$

Thus, E_b is given by:

$$E_b = E_t \sin\theta / \left\{ \left(5/4 - \frac{9R^2}{h^2}\right) \sin2\theta - 2\sin\theta \right.$$
$$\left. + \ \theta \left(\frac{12R^2}{h^2} \ [3/2 + 2\cos^2\theta - 2\cos\theta] + 1/2\right) \right\} \ .$$

and unit length having a curved segment of length a and a straight section of length $(1 - a)$. The curved section is composed of three arcs of a circle of radius R and subtending a total angle of 4θ.

4. Analysis

4.1. Modulus
If the effective Young's moduli* of the straight and curved sections are respectively E_t and E_b, the ribbon modulus, E_r, will be given by:

$$E_r = \frac{E_t E_b}{aE_t + (1 - a) E_b} \ .$$

As $E_b \ll E_t$ and even in high modulus fibres, the fraction of straight material $(1 - a)$, is small, this expression may be approximated to:

$$E_r \simeq E_b/a \ .$$

The modulus of the curved section may be derived by computing its strain, ϵ, when a given stress, σ, is applied. Provided the angle (θ) is not too large ($\theta < 0.3$ radians), one may neglect the contribution of shear to the extension of the ribbon and so only the contributions to the strain produced by tension, ϵ_t, and bending, ϵ_b, need to be taken into consideration. Provided that R/h is greater than 10, these may be calculated by the application of Castigliano's theorem [13] to be:

Because the distribution of a, h and θ is unknown, a quantitative description of the variation of the fibre modulus in response to changes in these parameters cannot be calculated exactly but some qualitative predictions of their influence can be made, since a general increase or decrease in ribbon modulus would be expected to exert a similar influence on the fibre modulus.

In order to ascertain whether this model provides a satisfactory explanation for the changes in physical properties observed when different heat-treatment temperatures are employed, one must be able to describe the structural changes which take place under these conditions. Essentially, the thickness of the ribbons [9, 10] and their average alignment parallel to the fibre axis [7, 8, 11] (as measured by X-ray diffraction techniques) have been shown to increase with an increase in heat-treatment temperature. The increase in orientation can be accounted for by a straightening of the ribbons, in which the curvature of the curved sections is gradually reduced. This would mean a gradual reduction of the angle subtended by the curved section, θ, but the fraction of curved material, a, may be assumed to remain almost constant.

To calculate the influence of a change in the relevant parameters on E_b, the simplifying assumption that the arc length of the curved segment remains constant was made (that is to say $R\theta = l$, a constant). As one would not expect the graphite basal planes to be extended during unwrinkling and no change in their internal spacings is indicated by X-ray diffraction, such an assumption appears to be

*The term "modulus" refers to the ratio of stress to the strain produced by a component and is not used in the sense of some intrinsic property of the material forming the component. Thus, "modulus" in this paper depends on the conformation of the material as well as its intrinsic properties, e.g. for a bent ribbon it is the ratio of the longitudinal stress applied to the ribbon to the longitudinal strain resulting from the unbending of the ribbon.
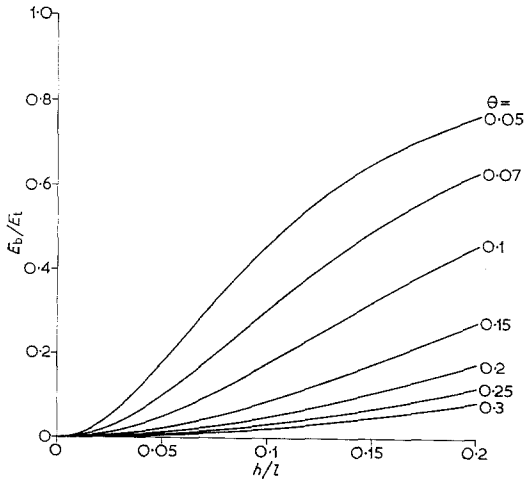
Figure 2 Variation of the modulus of the curved section, E_b (relative to the tensile modulus, E_t), with ribbon thickness, h, and angle, θ, over a range of values typically found in carbon fibres.

justified. When this simplification is made, the expression for E_b becomes

$$E_b = E_t \sin\theta / \{[5/4 - 9l^2/(h^2\theta^2)] \sin 2\theta - 2\sin\theta + \theta[12l^2/(h^2\theta^2)(3/2 + 2\cos^2\theta - 2\cos\theta) + \tfrac{1}{2}]\}.$$

The influence of h and θ on E_b is shown in Fig. 2. It can be seen that E_b increases with an increase in h or a decrease in θ, both of which are known to accompany an increase in heat-treatment temperature.

Thus, the behaviour of the model is in accord with the increase in modulus with increased heat-treatment temperature which is observed in practice. The contribution of the increase in ribbon thickness to the increase in modulus is noteworthy as this possibility does not seem to have received attention elsewhere.

4.2. Strength

If one assumes an equal strain condition to exist between ribbons, the stress carried by each ribbon will be proportional to its modulus and will be:

$$\sigma_r = \frac{E_r \sigma_f}{E_f} \sim \frac{E_b \sigma_f}{aE_f}$$

where E_f is the fibre modulus and σ_f is the stress applied to the fibre. However, in order to balance the moment produced by the tension applied to the straight section, the stress is not evenly distributed in the curved section with the maximum stress being produced at its concave

edge. The value of this maximum stress, σ_{max}, is given by [12]:

$$\sigma_{max} = 6\sigma_r \frac{R}{h} (1 - \cos\theta) .$$

If fracture is initiated when the maximum stress exceeds some critical value, σ_0, then at fracture

$$\sigma_0 = 6\sigma_R \frac{R}{h} (1 - \cos\theta)$$

where σ_R is the ribbon stress at fracture. The fibre stress at fracture, σ_F, is thus given by

$$\sigma_F = \frac{aE_f \sigma_R}{E_b}$$

$$= \frac{aE_f \sigma_0}{E_b} \frac{h}{6R(1 - \cos\theta)}$$

$$= aE_f \sigma_0 F(\theta, h/R)$$

where $F(\theta, h/R) = h/[6RE_b (1 - \cos\theta)]$.

The variation of $F(\theta, h/R)$ with θ and h/l ($l = R\theta$) is shown in Fig. 3.
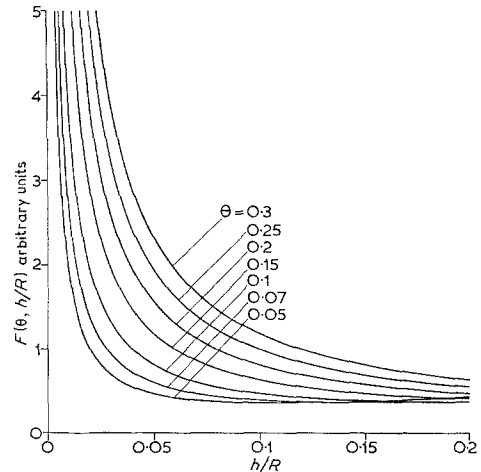

Figure 3 Variation of $F(\theta, h/R)$ with θ and h/l over a range of values typically found in carbon fibres.

On the basis of this information, one can attempt to relate the change in fracture stress, σ_F, to changes in other parameters as the heat treatment temperature is increased. Both the fibre modulus, E_f, and the ribbon thickness increase fairly linearly with increasing heat-treatment temperature – E_f increasing from about 35×10^6 psi for treatments at $1500°C$ to about 70×10^6 psi for treatments at $2800°C$ and h increasing from an average of about 2 nm to

an average of 6 nm under the same conditions [1, 6, 9]. Thus, when progressing from 1500 to 2800°C one would expect E_f to double, thus increasing the fibre strength, but (as can be seen from Fig. 3) this would be more than offset by the large decrease in $F(\theta, h/R)$ produced by the increase in h and decrease in θ brought about. The effect due to the decrease in $F(\theta, h/R)$ would be greatest for small values of h since the rate of change of $F(\theta, h/R)$ decreases with increasing values of h. One would, therefore, expect that the rate of strength loss with increasing heat-treatment temperature would be greater for lower temperatures and this is found in practice. The rate of strength loss is greatest for fibres treated to lower treatment temperatures and becomes almost zero for treatment temperatures in excess of 2000°C [1,6] when the decrease in $F(\theta, h/R)$ would be balanced by the increase in E_f.

An increase in strength as well as modulus accompanies stress-graphitization [14, 15]. In this case, h is increased considerably while θ is decreased [10]. The strength increase would be due to the values of h becoming so large that the decrease in $F(\theta, h/R)$ produced by the increased thickness and decreased angle would be less than the increase in E_f produced by these same changes.

One would also expect failure by this mechanism to have the same statistical properties as flaw initiated failure. The probability of finding a curved section where the maximum stress is sufficiently great to cause failure at a particular load is obviously a function of the fibre volume and so one would expect a Poisson distribution of strength with respect to length to result, causing the strength to decrease with increasing sample length. Thus, the proposed fracture model is in accord with the observed decrease in strength with sample length [5] which was referred to above when discussing the possible contribution of flaws to the fracture mechanism.

5. Conclusions

Both the strength and modulus properties of carbon fibres treated to above 1200°C are explicable in terms of the fibre fine structure alone provided that the contribution of bending

to the unwrinkling of the ribbons is taken into account. The loss in strength which accompanies an increase in fibre modulus as the heat-treatment temperature is increased above 1500°C can then be seen as a consequence of the increase in ribbon thickness which takes place under these conditions. This is not to say that flaws are not present or that, under certain circumstances, they may influence fracture. But, in general, the strain at fracture for fibres treated to above 1200°C appears to be too low to involve surface flaws and the density of internal flaws appears to be too low to exert a general influence on their fracture properties.

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