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The strength of pitch-based carbon fibre at high temperature

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The strengths of some high modulus pitch-based carbon fibres have been determined up to 1300 °C in both air and nitrogen atmospheres. The fibres possessed Young's moduli of 700 GPa and were 10 μm in diameter. The strength of the fibres was seen to be gauge length dependent but to a lesser extent than is usual with PAN-based carbon fibres. The fibre strength was observed to increase with temperature as did the Weibull modulus.

1. Introduction

High performance carbon fibres can be made from a variety of precursor fibres [1]. The most common and successful route employs polyacrylonitrile (PAN) precursors which gives carbon fibres which possess Young's moduli typically between 240 and 400 GPa depending on the pyrolysis conditions used [2]. This class of fibre has found wide use in the aerospace and sports goods markets. The production of PAN-based carbon fibres requires, therefore, the manufacture of an organic fibre, itself a relatively costly procedure and then its conversion to carbon with a carbon yield of around 45%.

The use of pitch, either obtained as the residue of oil refining or from coal as a residue from the coking process, has long been considered as a potentially economic route for producing carbon fibres [2]. The starting product, pitch, is cheap and widely available and its high carbon content clearly indicates a high conversion factor usually given as being around 85%. Carbon fibres made from pitch have been available for almost as long as PAN-based fibres. Their promise of being cheaper has not been fulfilled but they have been made with extremely high moduli albeit with very small breaking strains.

The last few years have been a period of intense activity by a number of Japanese companies in developing improved carbon fibres by the pitch route. The process which entails the conversion of the pitch into a mesophase or liquid crystal state has been refined so that there now exists a number of sources of this type of fibre with improved handling characteristics.

Carbon fibres have high specific moduli and strength and retain these properties to very high temperatures in inert atmospheres. They are therefore used as reinforcements at high temperatures, however there are few reports on their behaviour under high temperature conditions because of the experimental difficulties involved.

2. Experimental details

Single carbon fibres were tested in tension using a universal fibre tester fitted with a tubular furnace capable of operating up to 1400 °C described in detail elsewhere [3]. As the tests did not require cyclic loading the vibrator was removed from the fibre tester and the grips attached to the chassis of the machine. At room temperature, which was controlled at 23 °C and 50% r.h., the fibres were fixed horizontally in the two clamps after being glued onto card frames. The frames were cut after mounting of the fibre and the load and deformation of the fibre monitored and the signals feed directly into a personal computer which calculated the material parameters.

The gauge lengths used at room temperature were 10, 25, 50, 100 and 150 mm and approximately 20 fine fibres were broken with each gauge length.

Tests at high temperatures were conducted with a gauge length of 25 mm and the fibres cemented onto alumina rods over a length of 30 mm. The cement used was a high temperature ceramic cement and this allowed both the fibre and the grips to be introduced into the furnace which was positioned so as slide over the alumina rods to allow specimen mounting. In this way the fibre was subjected to uniform heating over its whole gauge length. The tests in nitrogen were conducted with a continuous flow of nitrogen passing over the fibre. There were approximately 25 fibres tested at each temperature.

The fibre diameters were measured using a Watson image shearing eyepiece attached to a binocular optical microscope.

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The fibres examined in this study were the HM-70 fibres from Petoca Co.

3. Results

The fibres were found to have an average diameter of 10 μm with little variation between fibres.

The strength of the carbon fibres tested at 23 °C was seen to fall only slightly with gauge length as can be seen from Fig. 1. The scatter in the results increased however with gauge length and this led to a fall in the Weibull modulus, as can be seen from Fig. 2.

The tests conducted at high temperatures in nitrogen revealed a slight increase in strength above 1000 °C, as is generally the case with carbon, and these results are shown in Fig. 3. The Weibull modulus increased with temperature as is shown by Fig. 4. It can be seen from Fig. 5 that the Young's modulus of the fibre also increased with temperature and as Fig. 6 reveals the strain to failure decreased slightly above 1000 °C.

4. Discussion

The experimental results confirm the necessity to test carbon fibres at a uniform temperature over the entire gauge length. Other fibres which can operate at high temperatures have been tested with the end grips at room temperature, or at least at a much lower temperature than that of the central region of the gauge length [4]. With most fibres this arrangement ensures failure in the central region as strength falls with temperature. Clearly this is not so with carbon fibres so that the whole gauge length should be at the operating temperature, including the grip regions. The additional experimental difficulties that this imposes is partly compensated by the greater accuracy which becomes possible when determining strain. This combined with the low scatter in fibre diameter helped in analysing the results.

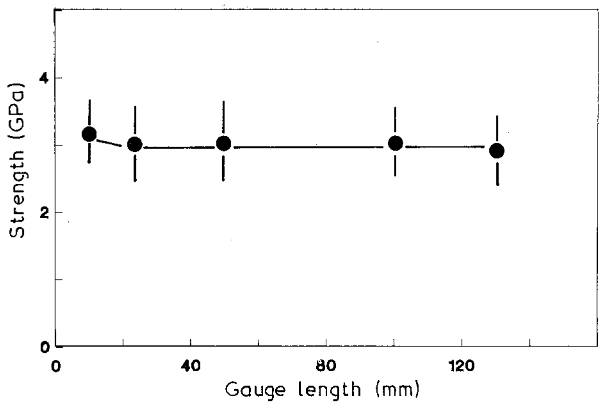

Figure 1 Fibre strength fell only slightly as the gauge length was increased.

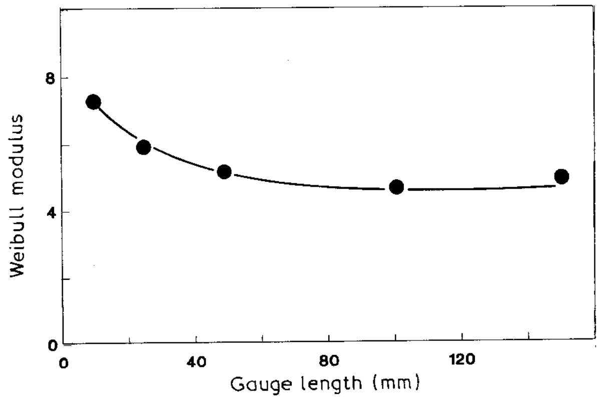

Figure 2 Fibre strength showed increasing scatter as gauge length increased and this led to a fall in Weibull modulus.

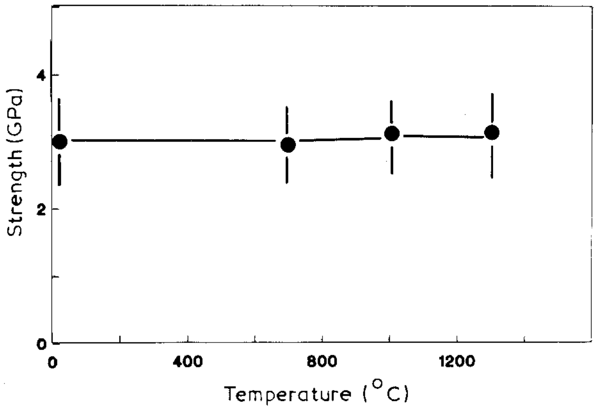

Figure 3 A slight increase in fibre strength was observed above 1000 °C.

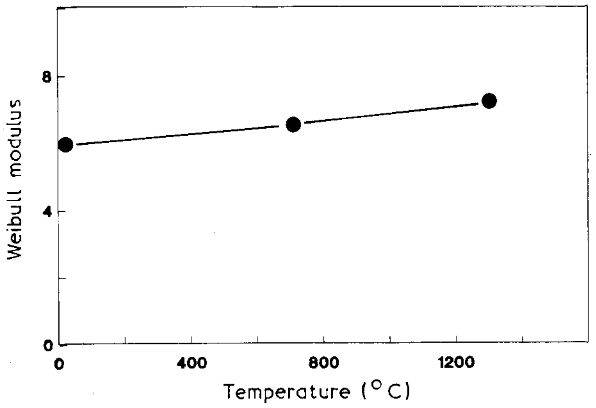

Figure 4 Weibull modulus increased slightly as the temperature increased.

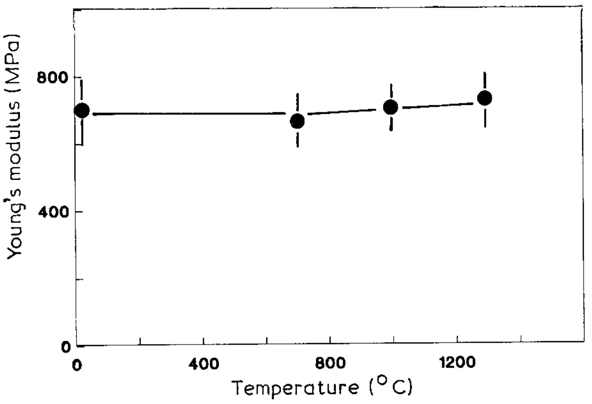

Figure 5 The Young's modulus of the fibre increased slightly as temperature increased.

The mean fibre strength was seen to be little affected by gauge length at 23 °C and less than observed with

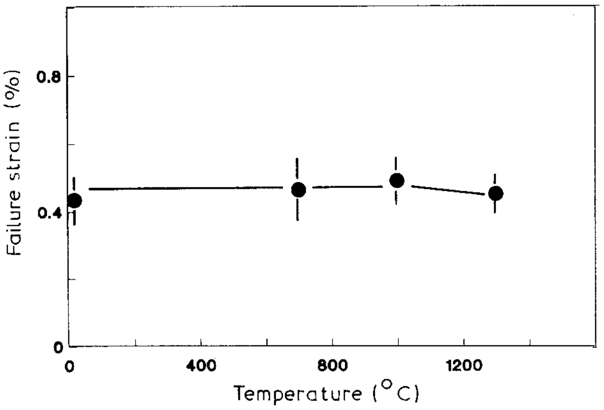

Figure 6 Fibre strain to failure decreased slightly as the temperature was raised.

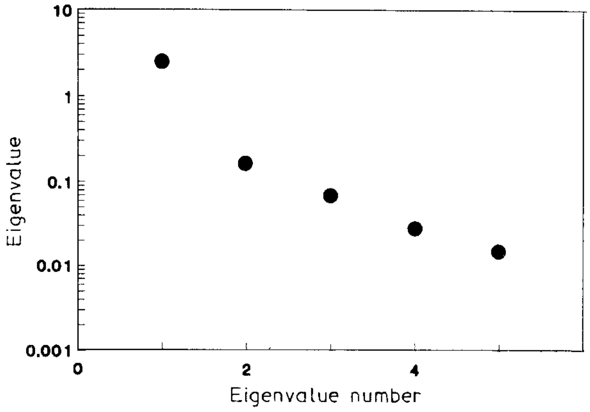

Figure 7 The number of significant non-zero Eigen values can be seen to be three suggesting the possibility of three defect populations in the fibres.

PAN-based fibres [5] however there was a considerable fall in Weibull modulus. An explanation for this latter observation could be that more than one defect population exists in these fibres and that their relative importance varies with length [6]. In order to examine this possibility further the results were analysed using a self consistent Weibull analysis of the fibre strength distributions as described by Beetz [7]. Self consistency is obtained by this method by determining an optimum fit to the experimental tensile strength data obtained at the different gauge lengths. The parameters of the probability distribution are considered to be intrinsic fibre properties and this analysis states that the probability of the fibre of length L surviving to a stress σ is given by the sum of the probabilities of the individual survival probabilities for each of the n defects so that

$$P = \sum_{i=1}^{n} X_i P_i \tag{1}$$

where $P_i = \exp[-L(\sigma/\sigma_{0i}]^{m_i}$

such that σ_{0i} is material parameter which is a function of the type of defect and m_i is the Weibull modulus associated with that defect population.

It should be noted that

$$\sum_{i=1}^{n} X_i = 1 \tag{2}$$

The Weibull parameters σ_{0i} and m_i are considered to be independent of gauge length for each type of defect. It is necessary to find a single set of m_i and σ_{0i} parameters which satisfy the experimental results. This is achieved by allowing X_i to vary with gauge length during the calculation and then the most probable set of m_i, σ_{0i} and X_i determined. For a detailed descriptions of this method see Beetz [7]. Mathematically the analysis requires the determination of the probability of failure P_{0i} for the ith gauge length at tensile strength σ so that if $P_{\sigma k}$ is the probability of failure due to the kth defect in an interval $\Delta\sigma$ about σ and n_{ki} is the number of kth defects in the ith gauge length

$$P_{\sigma i} = \sum_{k=1}^{m} P_{\sigma k} n_{ki} \quad \sigma = 1, \ldots, \mathrm{N} \quad i = 1 \tag{3}$$

In order to obey this condition it is necessary to determine a set of non-zero eigenvalues which allows the conditions described in Equation 3 to be met. When the results were analysed in this way the number of eigenvalues significantly above zero was seen to be three, as Fig. 7 indicates. The fourth and fifth eigenvalues were less than 2% of the first eigenvalue. This suggests that three defect populations were controlling the fibre behaviour at room temperature. These could be large defects limited to large topographical irregularities at the surface and a smaller defect population at the surface related to the arrangement of the aromatic structural units, independent of the first as well as a third type of defect in the bulk perhaps related to pore size [6].

At higher temperatures at which the fibres were heated in nitrogen similar behaviour to that generally seen with carbonacious materials was observed. The strengths and Young's moduli both increased with temperature suggesting an improved alignment of the microstructure and possibly the release of residual shear strains in the fibres [9]. The Weibull modulus was found to increase with temperature which also suggests a modification of at least the surface structure. Such changes must alter the defects and defect populations as identified above as controlling failure at room temperature. Such changes must lead to a decrease in stress concentrations which would also contribute to an increase in strength but not to Young's modulus.

5. Conclusions

The experimental difficulties of testing single pitch-based carbon fibres at high temperatures have been overcome. The mechanical properties of the fibres increase with temperature at least up to 1300 °C. It is most likely that three independent defect populations control the behaviour of the fibres and that these defects are modified at high temperature to result in higher values of Weibull moduli.

Acknowledgement

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