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# A New Glassy Carbon Fibre

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It is shown that phenol-hexamine polymers may be extruded from the melt to produce fibres which may be carbonised to form fine high-strength glassy carbon fibres with a tensile strength of up to 2 $GNm^{-2}$ (300 000 lb $in^{-2}$) after 900° C heat-treatment. The fibres have a specific modulus of $\sim$ 5 Mm compared with $\sim$ 14 Mm for carbonised polyacrylonitrile fibres and $\sim$ 3 Mm for silica glass fibres. Both strength and modulus increase rapidly with decrease in diameter. The fibres are subjected to no special surface treatment after extrusion but electron microscopy indicates the presence of a thin textured sheath surrounding a true glassy carbon core in the final fibre. The fibres have the advantages of glassy carbon (inertness to chemical attack, resistance to abrasion) and give promise of a new range of cheap high-strength carbon fibres derived from coal tar fractions.

## 1. Introduction

Carbon fibres have been made by the carbonisation of different organic polymers [1–4]. Excellent mechanical properties of carbon fibres were obtained when it was discovered that texture could in induced in "polyacrylonitrile-carbon" fibres by stretching during oxidation prior to carbonisation [5]. These textured fibres are semi-graphitic and have high strength and modulus. They are being used in new technological developments, e.g. in turbine blades by Rolls-Royce Limited; however, the main drawback is their high cost.

It has been known for some time that a glassy form of carbon can be produced by the carbonisation of phenolic resins [6]. This glass is similar in mechanical properties to normal silica glass but is harder, much more inert to chemical attack, is substantially unchanged even at 3000° C, and has a lower density of only 1.4 $Mgm^{-3}$. In working on the carbonisation of coal by-products we have found it possible to make such a material cheaply and easily. We therefore decided to look into the possibility of making the glass in the shape of fibres. This paper outlines our process, an evaluation of the product, and gives our interpretation of the mechanisms of the process and the structure of the final fibres. It is based on our original patent [7]. Work on other fibres of a glassy nature has been announced independently by Yamada [8].

## 2. Experimental

### 2.1. Materials Used

Phenol was used throughout and was mixed with hexamine (hexamethylene-tetramine $(CH_2)_6N_4$) in air in molar proportions varying between 6:1 and 24:1 to produce typical phenolic condensation polymers. Hexamine may be dissolved in liquid phenol warmed above 60° C and this solution is stable provided that the temperature is kept below 100° C. Hexamine decomposes into formaldehyde and ammonia above 100° C with moisture present. At 104° C, a reaction occurs which produces a linear thermoplastic polymer with the structure indicated in fig. 1a. At temperatures above 140° C, if there is enough hexamine present, cross-links form between these chains to produce a thermo-setting resin with the structure indicated in fig. 1b. This carbonises to form a glassy carbon with a high porosity due to the entrapment of gases which are an unavoidable product of the carbonisation process unless special precautions are taken.

### 2.2. Extrusion Process

The phenol-hexamine first-stage polymer was formed in a stainless steel pot and heated to temperatures controlled between 120 and 135° C under nitrogen. The nitrogen pressure was increased so that the polymer was forced through an orifice at the bottom of the pot. The fibre was drawn in air by wrapping it around a rotating

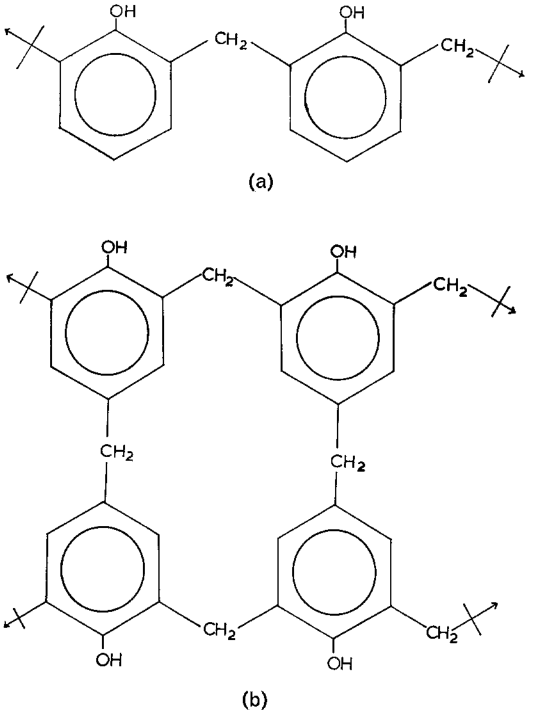

*Figure 1* (a) Structure of linear polymer of phenol-hexamine; (b) structure of resin of phenol-hexamine.

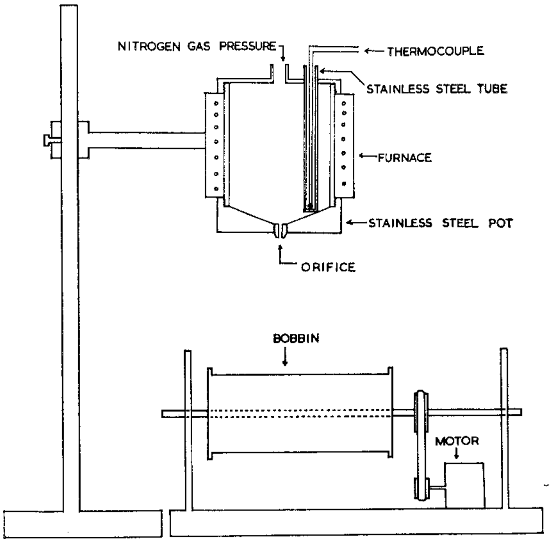

*Figure 2* Melt extrusion of phenol-hexamine.

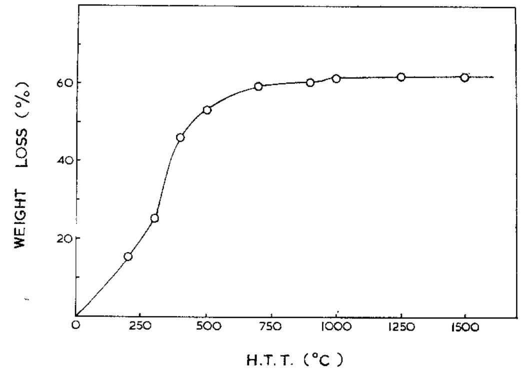

*Figure 3* Weight loss of phenol-hexamine fibre during carbonisation.

frame as shown in fig. 2. The speed of rotation of the frame and the diameter of the orifice govern the texture in the fibres and their diameter. In this way fibres of very large length can be drawn, with diameters of less than 20 μm.

### 2.3. Carbonisation Process

The fibres in our simple process were laid down on trays and heated slowly in nitrogen at about 1 °C min$^{-1}$ to 350 °C. Rapid increase was possible thereafter to a typical temperature of 900° C. Providing a critical extrusion temperature is chosen, fibre distortion and adherence to the tray can be eliminated; no special surface treatment is necessary. In fact, it was found that hardening the surface by ozonolysis and dilute acids only served to embrittle the final fibre.

Fig. 3 shows the weight loss of the fibres during carbonisation in an inert atmosphere. A significant weight loss takes place at heat-treatment temperatures between 300 and 400° C. The critical temperature for the resin-carbon transformation appears to be 350° C. The colour of the fibres also changes remarkably at these heat-treatment temperatures. The original amber colour deepens and the material changes suddenly at 350° C to an opaque black glass. A very broad (0002) band of carbon can be observed in the X-ray diffraction pattern of fibres heat-treated even at 400° C. The removal of methylene bridges and the growth of aromatic sheets can be observed by infra-red spectroscopy in fibres heat-treated at 350° C. Infra-red spectroscopic studies also show that the process is similar to the carbonisation of the phenol-formaldehyde system [9], catalysed by the decomposition product, ammonia.

Weight loss and dimensional changes in bulk glassy carbon become negligible with heat-treatments above 1000° C. At this temperature electrical resistivity also reaches a minimum (at ~ 1 mΩcm). Higher temperatures, even up to 2800° C, have little effect. It is therefore inferred that the carbonisation process is complete at 1000° C. This contrasts with the behaviour of soft cokes, which show changes at all temperatures up to 2800° C.

## 3. Structure and Mechanical Properties of the Carbonised Fibres

Very thin fibres as thin as 5μm diameter can be produced (measurement made by photomicrography). Measurements were made of the X-ray lattice parameters, crystallite sizes, Young's modulus and ultimate tensile strength of the fibres. Some of the data on mechanical properties were obtained at the Rolls-Royce Laboratories, Derby.

### 3.1. X-ray Diffraction Studies

A Debye-Scherrer camera was used to study fibres bonded together at both ends with Durofix, bundled into a special glass X-ray tube and crushed into powder.

Figs. 4 and 5 indicate the changes in interlayer spacing and crystallite size with heat-treatment temperature. The data show that the fibres consist for the most part of the extreme non-graphitising carbon known as glassy or vitreous carbon. Fig. 6a shows one example of the X-ray diffraction pattern of fibres heated to 2500° C. Fig. 6b shows an X-ray diffraction pattern of a commercial bulk glassy carbon; there is no essential difference. Fig. 6c shows a diffraction pattern of carbonised polyacrylonitrile fibre heated to 2500° C; it is clearly graphitised to some extent and is markedly textured. It is difficult to detect any such texture in our final fibres. However, a very thin graphitic layer is observed using transmission electron diffraction and microscopy, on the surface of our thin fibres heated to 2500° C. An example is shown in fig. 7. This should be compared with a thin section taken from the core of the fibre (fig. 8).

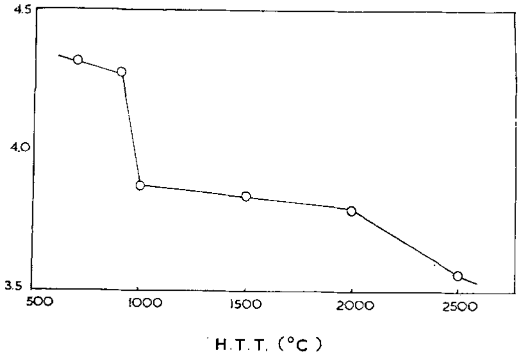

*Figure 4* Variation of interlayer spacing with heat-treatment.

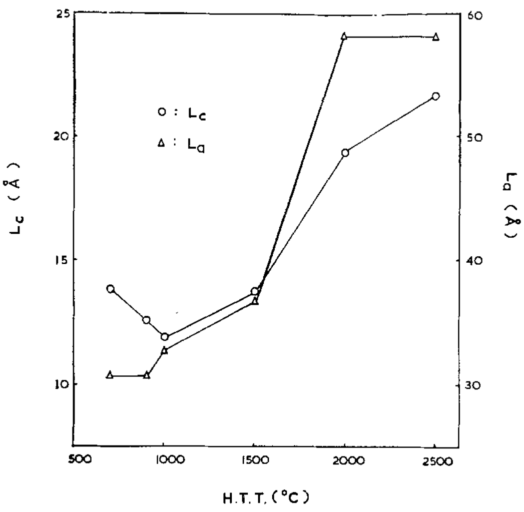

*Figure 5* Variation of crystallite sizes with heat-treatment.

This result indicates that the outer part of the fibre is much more textured and crystalline (after heat-treatment at graphitising temperature) than the inner part, so that we can perhaps regard the fibre as a two-component system consisting of an amorphous core surrounded by a textured, more crystalline, sheath.

### 3.2. Mechanical Properties of the Carbonised Fibres

Measurements of mechanical properties of fibres were made using an Ether tensile load cell and an Instron machine. It was found that both the ultimate tensile strength and Young's modulus were highly dependent on fibre diameter. This is shown in figs. 9 and 10, wherein decrease in diameter produces an increase in both strength and modulus, the greatest change appearing for diameters of less than 20 μm. Fibres of 5 μm diameter have a strength of 2 ± 0.3 $GNm^{-2}$ (300 000 lb) and a modulus of 70 ± 10 $GNm^{-2}$ ($10 \times 10^6$ lb $in^{-2}$). Since the density is only 1.4 $Mgm^{-3}$, this fibre has a specific modulus of ~ 5 Mm and a specific strength of ~ 0.15 Mm. (*Specific* modulus and strength are the ratios of the actual modulus and strength in $Mgm^{-2}$ to density in $Mgm^{-3}$ and have therefore the units of length.) This length serves to define the reinforcing properties of a fibre and to compare it with

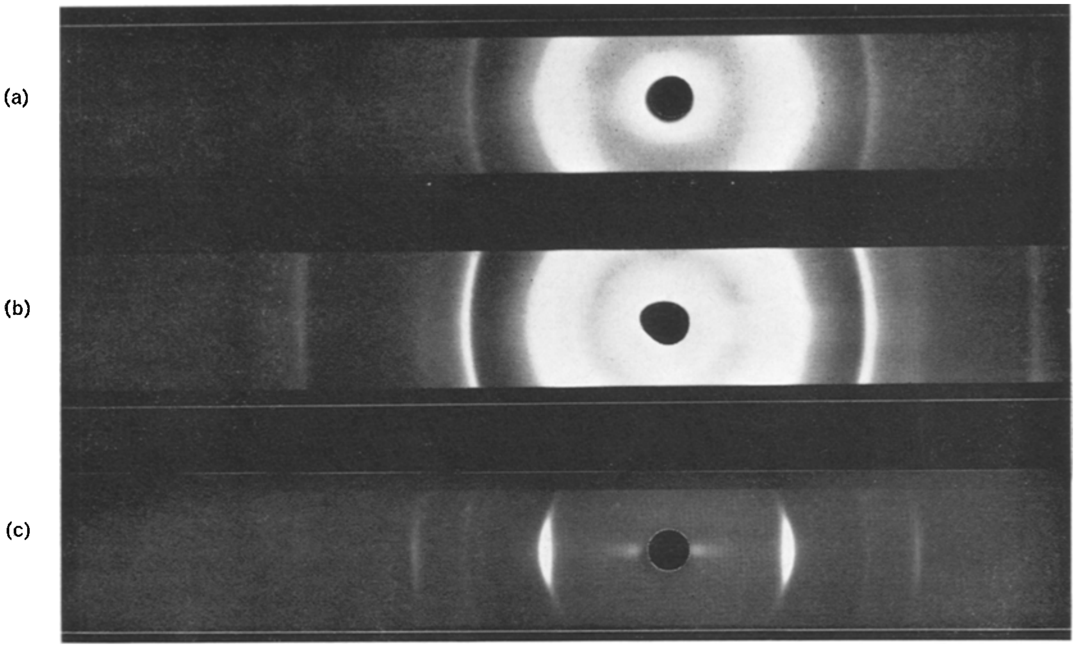

*Figure 6* (a) X-ray diffraction pattern of carbonised phenol-hexamine fibres heat-treated at 2500° C; (b) X-ray diffraction pattern of commercial glassy carbon; (c) X-ray diffraction pattern of carbonised polyacrylonitrile fibres.

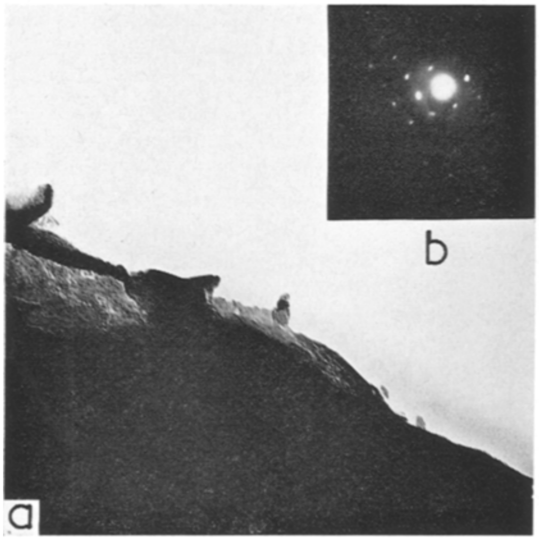

*Figure 7* (a) Electron micrograph of a thin layer in the surface of a fibre (× 16 300); (b) electron diffraction pattern of this thin layer.

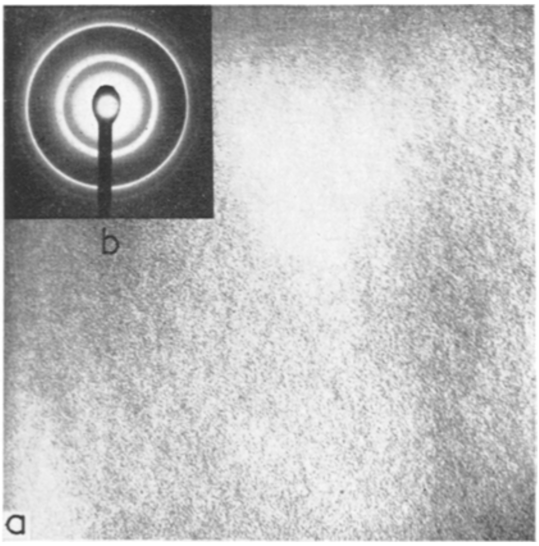

*Figure 8* (a) Electron micrograph of thin section from core of the fibre (× 16 500); (b) electron diffraction pattern of this thin section.

other fibres of different densities. Higher strengths and moduli are expected for thinner fibres.

## 4. Discussion

It has been shown that glassy carbon may be made in the form of fibres with high specific strength and modulus by a very simple process from a cheap phenolic resin. The values of both strength and modulus are considerably greater than for the bulk material (for which values are

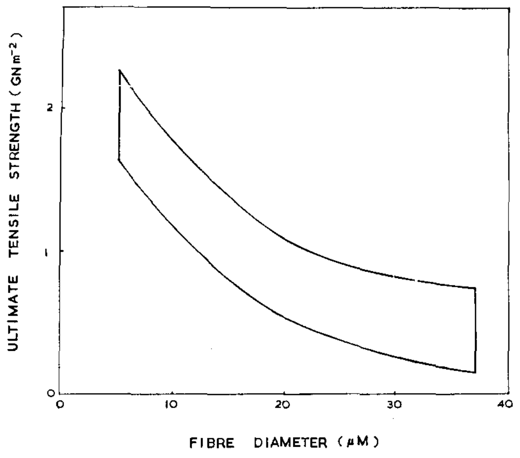

*Figure 9* Variation with fibre diameter of ultimate tensile strength of phenol-hexamine fibres heat-treated at 900° C.

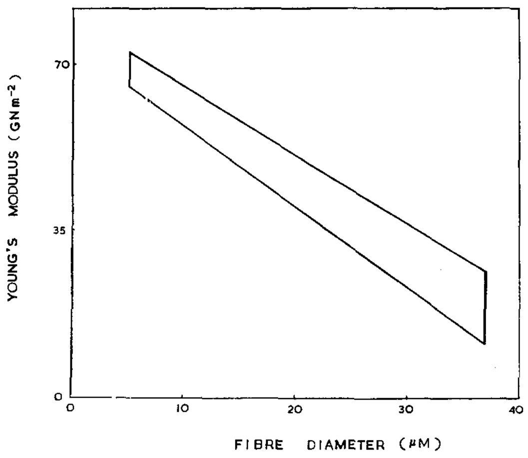

*Figure 10* Variation with fibre diameter of Young's modulus of phenol-hexamine fibres heat-treated at 900° C.

$\sim$ 0.06 $\text{GNm}^{-2}$ and $\sim$ 30 $\text{GNm}^{-2}$ respectively) and the thinner the fibres, the greater the values become.

The increase of the Young's modulus as well as the strength of the fibres with decrease in diameter is difficult to explain by assuming that the thicker fibres contain a greater population of surface cracks, as is assumed for silica fibres [10]. The glassy carbon fibres are harder and much more inert than silica glass fibres; they are therefore much less susceptible to surface abrasion. In any case, the presence of such cracks would not appreciably affect the elastic modulus, only the strength. We therefore attribute the increase in *both* these properties with decrease in diameter to the increase in the relative importance of the outer textured sheath in thin fibres less than 10 μm in diameter. It is appropriate here to conjecture how this outer layer is produced. As the precursor fibres are extruded they are textured by shearing and tensile forces from the constraint imposed by the orifice and from the pull of the rotating bobbin. The texture is frozen in the fibres by the rapid cooling to which they are subjected, this is easily detected by normal optical birefringence techniques. As the fibre is heated we know that this texture disappears, unless oxidation is allowed. Oxidation of the fibres occurs even at room temperature with time, witnessed as a deepening of the amber colour. It is therefore not unreasonable to assume that some oxidation occurs immediately the hot fibre (at 130° C) is exposed to air even momentarily and that this oxidation serves to set a texture locally at the surface by chemical bonds; this texture is carried through to the subsequent carbonisation. There is an optimum thickness for the effect of such a textured layer on mechanical properties since further premeditated oxidation of the precursor material in air and ozone only serves to embrittle the fibre product. It is interesting to note in this connection that the texture of polyacrylonitrile fibres is also set by oxidation during stretching.

This fibre or fibres of the same ilk should be very cheap to make from treated coal and oil tar fractions and should therefore find a niche in the present rapidly expanding market for ordinary glass fibres. It has advantages over silica glass fibres in that it is resistant to most chemical attack, apart from that of alkali metal vapours [11]. It has greater abrasion resistance and a higher specific modulus. It withstands very high temperatures and shows viscoelastic behaviour only at temperatures above 2500° C.

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## References

1. A. SHINDO, *J. Ceram. Ass. Japan* **69** (1961) C195.
2. M. M. TANG and R. BACON, *Carbon* **2** (1964) 211.
3. *Idem, ibid* 211.
4. S. OTANI, *ibid* 3 (1965) 31.
5. W. WATT, L. N. PHILLIPS, and W. JOHNSON, *The Engineer* May, 1966.

6. J. W. DAVIDSON, Brit. Patent 860, 342 (1961).
7. K. KAWAMURA and G. M. JENKINS, British Patent Specification No. 42539/68 (by National Coal Board) 1968.
8. S. YAMADA, The 8th Conference on Carbon, Buffalo, 1967.
9. K. OUCHI, *Carbon* 4 (1966) 59.
10. A. S. TETELMAN and A. J. MCEVILY JR, "Fracture of Structural Materials" (John Wiley & Sons, New York, 1967).
11. M. K. HALPIN and G. M. JENKINS, *Proc. Roy. Soc.*, **A313** (1969) 421.

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