

# DIRECT GRAPHITIZATION OF STABILIZED PAN FIBRES

*J. Mittal, O.P. Bahl and R.B. Mathur*

*Carbon Technology Unit, National Physical Laboratory, New Delhi 110 012, INDIA*

## Introduction

Polyacrylonitrile (PAN) in the fiber form is one of the most successful precursors for making high performance carbon fibres (1). In order to produce carbon fibres from PAN fibres, it has been established earlier, that PAN fibres must be stabilized at temperatures less than 270°C before carbonization upto of 1000°C and above (1-6). In the carbonization process the pyrolysis of stabilized fibres is generally carried out in two steps with two different heating rates. In the first step i.e. up to about 600°C, a low heating rate is recommended (less than 5°C/min.) primarily to make the mass transfer slow and also perhaps because of the inability of the structure of the stabilized PAN fibres to undertake higher heating rates. In the second step i.e. a temperature range beyond 600°C, higher heating rates (10 - 200 °C/min.) have been tried upto 1500 °C because of the lesser possibilities of damage to the structure due to exothermic reactions or the evolution of by products, since such reactions have already been completed up to 600°C (1,2).

Fitzer et.al (6) and various other authors have shown that 270°C is the optimum temperature of stabilization of PAN fibres. However, recent studies in this laboratory (7,8) have shown that the thermal stabilization of PAN fibres is not at all complete at low temperatures i.e., <300°C. PAN fibres stabilized in our laboratory at 350°C show different physical and structural characteristics than the one stabilized only upto 250°C (7,8). It was therefore assumed that such fibres might show different pyrolysis behaviour as well. Since it was proved that these fibres possess highly aromatized structure, very fast heating rate during carbonization as well as graphitization was attempted on these fibres and the results are presented here.

## Experimental

Courtelle 12 K PAN precursor tow of 1.2 d'tex was used for the present studies. Stabilization experiments were performed on the bench scale using set up described elsewhere (9). In the first set of experiments, PAN fibre tows were heated to 250°C at a heating rate of 1°C/min. An elongation of 10% was recorded. These stabilized tows, called sample 'A' were further heated in presence of air at 350°C for 1 minute. The fibre tow recorded no shrinkage

/elongation during 1 minute isothermal heating of the samples at 350°C, named sample 'B'. The difference in the structure of samples A and B has already been explained earlier (7,8). The difference being that sample B possesses a highly aromatic structure and almost 50% less hydrogen by wt. percent. Both the samples A and B were then directly carbonized in a single step with heating rate of 100°C/min. up to 2500°C in Astro graphitization furnace (Thermal Technology Inc. USA). A small number of filaments were removed from the tows after every interval of 100°C or 200°C in order to record variation in the mechanical properties with temperature between 500-2500°C.

Mechanical properties of the carbon fibres were measured on an Instron 1122 universal testing machine with a cross head speed of 0.5 mm/min. and a gauge length of 2 cm. An average of at least 25 single filament results for each sample is reported. Diameter of the fibres was measured to the accuracy of  $\pm 0.05\mu\text{m}$  on a Leitz microscope using Vicker's image shear eye piece. Density of carbon fibres was measured by the density gradient method developed by Pinoli and Ambrosio (10).

## Results and Discussion

Fig.1 shows that both the samples though show same trend in the increase in the tensile strength (T.S.) as well as Young's Modulus(Y.M.) there is a marked difference in the numerical values. Whereas for sample B the maximum value of T.S. is 3.7 GPa it is only 2.8 GPa in case of 'A'. Similarly the value of Y.M. of B is 425 GPa as compared to only 250 GPa for sample A. Not only this the sample A could not withstand such high heating rates beyond 1700°C, causing severe damage to its structure and became so brittle that it was not possible to separate individual filaments for testing. This is because of the understabilized structure of the fibres. The study therefore underlines the need for thermal stabilization of PAN fibres up to 350°C in order to undertake rapid carbonization or direct graphitization. As shown in the fig., beyond 1700°C sample B shows well known trend i.e. a decrease in T.S. and increase in Y.M.with further graphitization. It has been suggested that with increase in the heat treatment temperature ( HTT) there is a decrease in cross- linking

between the layer planes which makes them more mobile and finally results in a more perfect order of the graphitic planes. Failure of fibres in shear, therefore, results in lowering of tensile strength (11). However, according to Jones and Duncan (12), the decrease in strength is due to formation of basal plane cracks formed during coking, a manner similar to the formation of Mrozowski cracks in bulk graphite (13).

Variation in the density and the diameter of the sample B with heat treatment temperatures is shown in fig.2. It shows that most of the changes in the diameter and the density of the fibres 'B' takes place up to 800°C i.e the compaction of the structure takes place during early stages of carbonization. After 1000°C the improvement in the structure is through crystallite growth and elimination of defects because of decrease in the number of crystallite boundaries.

### Conclusion

The study shows that PAN fibres stabilized at 350°C can be subjected to carbonization and graphitization in a single step i.e. they can undergo direct graphitization to 2500°C with a heating rate of >100°C/min without sacrificing mechanical properties at all. On the other hand, fibres stabilized up to 250°C only show much lower mechanical properties comparatively when subjected to direct graphitization.

### Acknowledgment

The authors wish to thank Prof. E.S. Rajagopal, Director, NPL for his constant encouragement during the course of this work and his permission to publish it. One of

us (J. Mittal) is thankful to CSIR for the award of a research Associateship.

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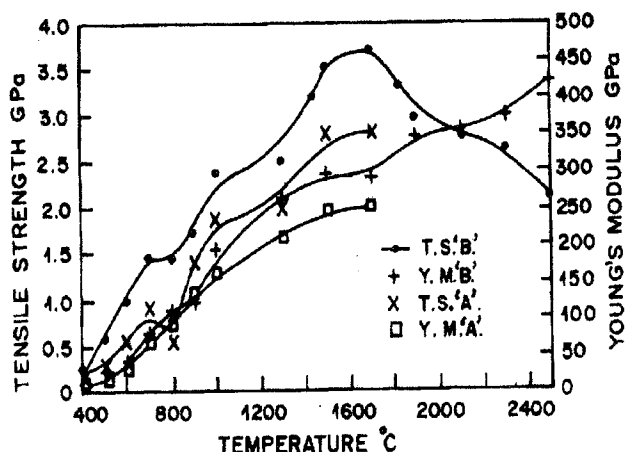


Figure 1. Change in tensile strength and Young's modulus of carbon fibres with heat treatment temperature.

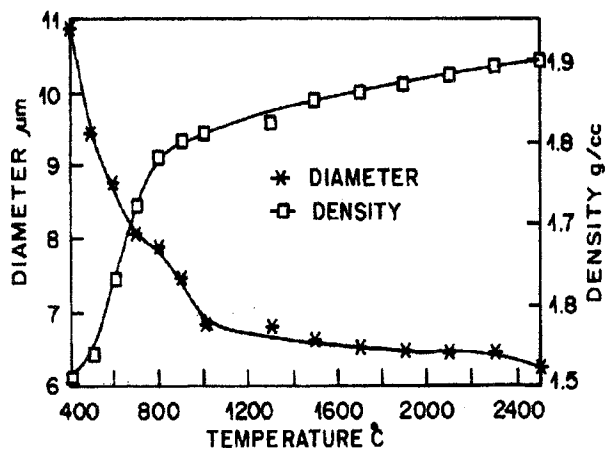


Figure 2. Change in diameter and density of carbon fibres with heat treatment temperature of sample 'B'.