

# STATUS OF CARBON FIBRES DEVELOPMENT

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## ABSTRACT

*A review of carbon fibres development all over the World is given with special reference to development in India. The present status of development as well as new approach to characterization are mentioned. The future course of development in this field is indicated.*

## INTRODUCTION

From time immemorial man always sought to develop lighter and stronger material. Cottrell [1] has suggested to what limit one can go in this direction. It is convenient to write the tensile strength for yield or fracture of a solid in the form

$$\sigma = aE. \quad (1)$$

Where  $\sigma$  is tensile strength,  $E$  is Young's modulus and  $a$  a constant. From atomic force displacement relations we expect the value  $a = 0.1$  for almost all solids. The ideal strength of a solid is therefore cannot exceed one tenth of its elastic modulus. Hence the best method to select a solid of ideal specific strength is to select them on the basis of their elastic constant and density. In practice however we are able to obtain in general  $a = 0.001$ . This is because of defects in solids in the form of dislocations and voids which cannot be avoided in engineering practice. These defects contain stress concentrations. One way to reduce the defects is to make solids in the form of fibres. In such cases  $a = 0.02$  could be achieved. It is in fact already achieved in fibre glass and strongest steel wire. Graphite whiskers also have a value of  $a = 0.02$  though they cannot be obtained in the form of fibres. But if we want light and strong materials, then carbon fibres are the only answer. Even here only a value of  $a = 0.01$  could be achieved at present.

*Precursors.*—In order to make carbon fibres it is better to take precursors in the form of fibres and carbonize them in an inert atmosphere and further graphitize them in order to get better modulus. There are three essential conditions which have to be fulfilled before any precursor can be made into carbon fibres. Firstly the alignment of the crystallites or fibrils in the precursors along the fibre direction should be as perfect as possible. Secondly formation of a polycyclic structure of carbon atoms in the benzene type of hexagonal ring should take place before complete dehydrogenation, and thirdly the fibres must be capable of being stretched after the fusion of carbon atoms. The first and third condition are self-evident. The second condition is important because some hydrogen atoms should remain attached to carbon in the fused ring so that on further dehydrogenation those carbon atoms associated with hydrogen atoms previously get unpaired electrons which make adjacent carbon atoms in the rings join making a parallel two-dimensional structure of carbon ring.

*Carbon Fibres from Cellulose Precursors.*—The first carbon fibres though of low strength and modulus were made by Tang and Bacon [2] who carbonized fortison 36 cellulose fibres (used for tyre coras). They heated these precursors at 40° C per hour in a slow flow of argon up to 1000° C. They postulated a multi-stage mechanism for the conversion of cellulose to carbon

- Stage I Physical desorption of water (25–150° C).
- Stage II Dehydration from the cellulose unit (150–240° C).
- Stage III Thermal cleavage of the cyclic linkage and scission of other C—O bonds and some C—C bonds *via* a free radical reaction (240–400° C).
- Stage IV Aromatization (400° C) and above.

One noteworthy feature of these investigations is that from X-ray diffraction analysis it was found that the memory of the starting structure persists through the entire pyrolysis process in spite of the fact that after heat treatment to a temperature of 300 to 400° C the X-ray pattern indicates an apparently completely amorphous structure. One possible explanation for this could be that the cellulose structure is first split up and then in the carbonization stage after fusion of carbon rings they recombine to give the original structure. Roger Bacon [3] has given a complete review of the carbonization and graphitization of cellulose fibres. The process involved for continuous production contain the following steps. The first is the

heat treatment process. It is done at 300 to 400° C in a reactive atmosphere such as air or oxygen, chlorine or hydrochloric acid vapour. They all seem to promote dehydration of the cellulose structure and to inhibit the formation of tars which tend to make the fibres stick to each other and make them brittle. This is further improved by creating more diffusion rates by use of impregnants prior to heat treatment. The impregnants include nitrogenous salts of strong acids or acidic salts, metal halides and various derivatives of phosphoric acid. All of these impregnants are well-known flame retardants. They also serve as carbonization promoters speed reaction rates and improve carbonization yields. Properly heat treated rayon can be carbonized from 1000° C to 1500° C in times considerably less than one minute. The strength and modulus of such carbonized commercial fibres are at best  $100 \times 10^3$  psi and  $6 \times 10^6$  psi respectively. The low yield of carbon fibres at best 30% is responsible for the low strength. Since these fibres do not become plastic after the fusion of carbon rings during the carbonization stage, these cannot be stretched. Hence the Young's modulus remains low. After graphitization to 2800° C the Young's modulus increases only to  $10 \times 10^6$  psi but the strength becomes only  $68 \times 10^3$  psi. But if the stretching is done at this temperature, where they become plastic, the modulus can be increased. At the same time strength also get increased. Roger Bacon<sup>3</sup> reports a modulus of  $30 \times 10^6$  psi at 50% stretch at 2800° C. The strength at this stretch becomes  $80 \times 10^6$  psi. By stretching further one can get higher modulus and strength. In fact thornal 75 of Union Carbide has a modulus of nearly  $75 \times 10^6$  psi. But for economic production stretching at high temperature is not feasible. Further for producing carbon fibres from rayon precursors, we have to depend on the production of these precursors which change from time to time because they are produced for different purposes. Everytime a change is made in precursor production complete change has to be made throughout in carbonization. So unless the precursors are produced just for conversion into carbon fibres, there is no use relying on these precursors. It is this difficulty combined with the uneconomical stretching at high temperature makes carbon fibres from cellulose precursor become obsolete. Bahl and Manocha [4] in India produced carbon fibres from century rayon precursors going up to 1000° C alone, having a strength of  $100 \times 10^3$  psi and a modulus of  $6 \times 10^6$  psi.

*Carbon Fibres from Pan Precursors.*—If some way is found to make the carbon fibres to be stretched after formation of a polycyclic structure at a lower temperature, then the fibres will have sufficient strength and modulus at economic production. Polyacrylonitrile precursors belong to this

category. These fibres however melt during carbonization and therefore they are oxidized to provide cross linking and prevent them from melting during carbonization. Shindo [5] was the first to oxidise and carbonize PAN precursors. Going up to  $1000^{\circ}\text{C}$  only he obtained a modulus of about  $20 \times 10^6$  psi and a strength of  $140 \times 10^3$  psi using a copolymer containing about five per cent of methyl acrylate. It was later on found by Watt [6] that oxidized fibres become plastic after formation of a polycyclic structure and therefore can be stretched at this stage itself. By using this technique Watt [6] obtained a modulus of  $30 \times 10^6$  psi and the strength of  $300 \times 10^3$  psi going up to  $1200^{\circ}\text{C}$  alone. Morgans produce commercial carbon fibres of the above properties, which are called type II carbon fibres. Stretching of oxidized PAN is not new. In order to produce flame-proofed filaments and textiles from PAN by oxidation, it was found desirable to control exactly the exothermic reaction between  $15^{\circ}\text{C}$  and  $350^{\circ}\text{C}$  and to minimize the shrinkage by mechanical means by tension [7]. The yield of carbon fibres from PAN precursors can be as high as 60%. This high modulus at a lower heat treatment temperature made possible by the fact that PAN in fibre form can be produced with a high degree of molecular orientation and these can be stretched after fusion at a relatively lower temperature of about  $200^{\circ}\text{C}$  economically. Moreton [8] found that stretching the fibres in the spinning stage increases the Young's modulus. The process simply consists as follows. Tows of PAN fibres are first passed through an air oven maintained at  $220^{\circ}\text{C}$  for a few hours, when they turn back. The differential speeds of incoming fibres and outgoing fibres sustained by two motors gives the necessary stretching. The oxidized fibres are then carbonized to  $1000^{\circ}\text{C}$  in an inert atmosphere and heated to temperature between 1500 and  $2500^{\circ}\text{C}$ . By going up to  $2500^{\circ}\text{C}$  the modulus can be increased to  $60 \times 10^6$  psi but the strength is decreased to about  $200 \times 10^3$  psi. Both the strength and modulus can be increased further by hot stretching at  $2500^{\circ}\text{C}$ .

*Oxidation.*—Figures 1 and 2 taken from Watt's paper describe the structural changes due to oxidation and carbonization respectively. However these can be taken only as a rough idea and still today no satisfactory model of structural change is available. The closest model of the oxidized structure is given by Clark and Bailey [9] which is represented in Fig. 3. The authors say that the oxidized fibres is aromatized as contrasted to fibres treated in an inert atmosphere where they are merely cyclized but not aromatized. When we say that a structure is aromatized they should have benzene type ring with three alternate double bonds which resonate into two different sequences. Figure 3 does not indicate the structure expected

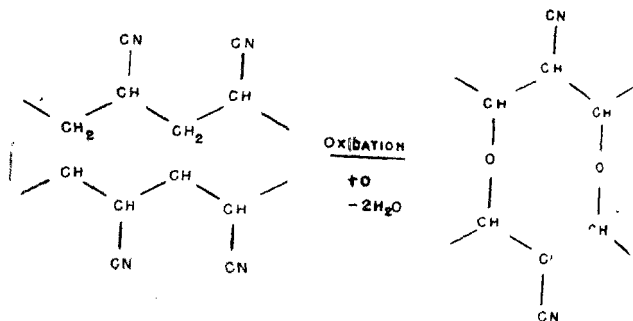


FIG. 1. Oxidation of PAN fibres : Oxygen forms a bridge linking two PAN molecules and water is liberated.

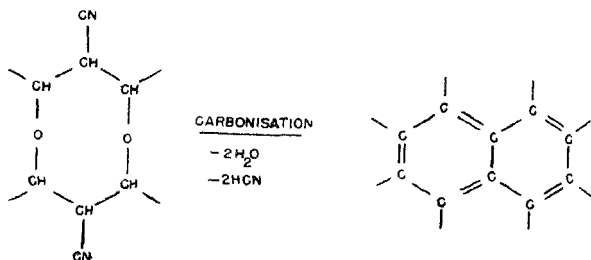


FIG. 2. Formation of a carbon ring structure by carbonizing oxidized PAN fibres. The carbon rings will have an orientation which is dependent on that of the original PAN chains and their subsequent oxidized form.

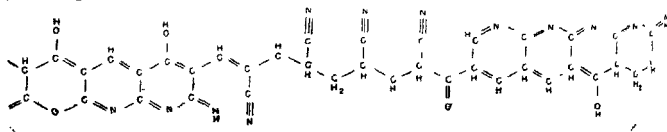


FIG. 3. Structure of oxidized PAN fibres heated to 225°C in air for 5 hours.

of an aromatized structure. Further they say that the structure given in Fig. 3 was derived from infra-red analysis. But the infra-red analysis given by the authors do not tally with the structure given. So we are back again to the question as to what oxygen does to the original structure of fibres. Verma *et al.* [10] give more comments on Clark and Bailey's paper.

Lot of work has still to be done to understand the oxidation stage. Perhaps it is not important to have a structure of oxidised fibres. It is more important to know what oxygen does. Fitzer and Muller [11] discuss through infra-red and DTA analysis that oxygen influences the cyclization in two opposite directions (a) the frequency factor is increased. Oxygen acts as inhibitor for the formation of activated centers and (b) the activation energy is increased. Oxygen acts as inhibitor for cyclization. The main parts of cyclization and dehydrogenation reactions take place simultaneously. Oxidation reactions precede cyclization but are slower during thermal treatment of PAN in air. Oxidation reaction continue even after cyclization is complete. More detailed work on this has been presented by Fitzer and Heym [12]. One way of looking at the process in oxidation is to say [13] that oxygen breaks the hydrogen bonds in the original structure (hydrogen is released in the form of water vapour) thus breaking the chains resulting in unpaired electrons at the edges of broken chains. Thus one can get electron spin absorption as the time of oxidation proceeds, to go up. These broken chains after aligning parallel to the fibre due to stretching can join together with the unpaired spins at the edges of adjoining chains pairing. This will lead to the constancy of spins after some time of oxidation due to the opposing tendencies of breaking and rejoining or a slightly lower absorption if the second process predominates. Finally when all the oxygen is used up in releasing water vapour, further oxygen merely is chemically adsorbed showing an oxygen sensitivity which drastically reduces the spin absorption. Sootha and Tripathi [14] has actually shown that electron spin absorption behaves in this manner. Figure 4 gives the ESR absorption (relative) with oxidation time of PAN fibres at different times. This increase in absorption in the beginning stage of oxidation is not shown when PAN fibres are treated in inert atmosphere or in vacuum. This is paralleled with the strength of oxidized fibres with time of oxidation. The strength does not fall as contrasted with oxidized fibres, when PAN fibres are treated in an inert atmosphere. This clearly shows the role of oxygen in breaking the chains in the initial stage of oxidation thus contributing to lowering of strength. Figure 5 gives the strength *versus* time of heat treatment on oxygen and nitrogen atmosphere taken from reference [15]. These results will be further strengthened if one measures the chain length and molecular weight distribution as the time of oxidation proceeds and correlate it with ESR absorption and strength.

**Carbonization.**—When the oxidized fibres are further heated in an inert atmosphere the following reaction as represented in Fig. 6 takes place. As is evident from this figure the  $H_2$  molecule attached to carbon

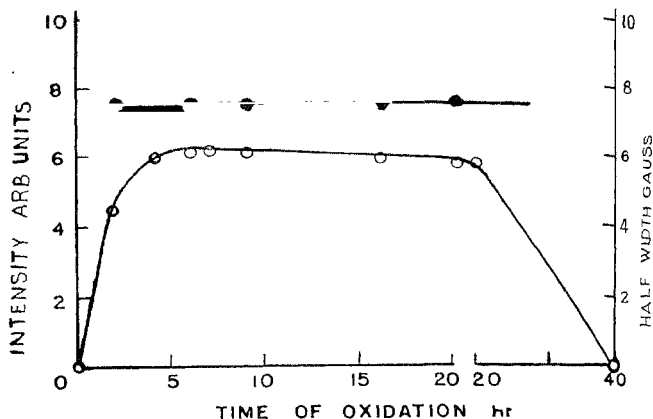


FIG. 4. Variation of intensity and half width of the ESR adsorption line with time oxidation at 205°C of PAN fibres at room temperature.

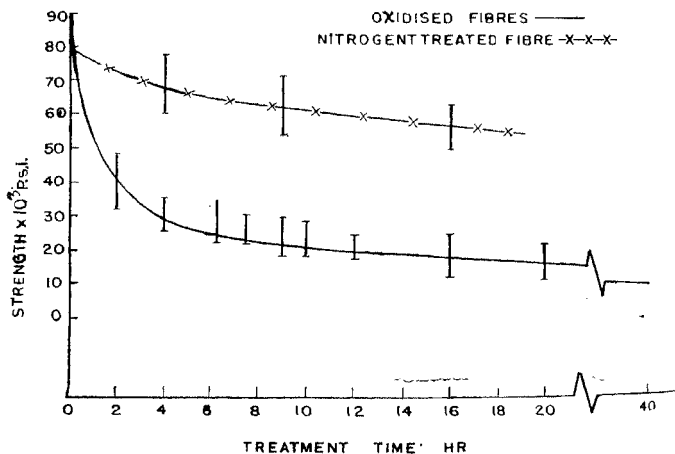


FIG. 5. Variation of tensile strength of oxidized and nitrogen treated fibres with different temperature time at 205°C.

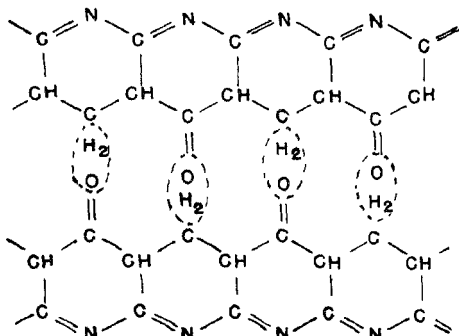


FIG. 6. Cross linking by inter molecular elimination of water.

in one chain reacts with the oxygen bonded to carbon in the adjoining chain, coming out as water vapour. This process creates cross linking between the chains and increases strength. If the carbonization is done for oxidized fibres oxidized at the earlier stages of oxidation water vapour elimination creates cross linking and the strength rises. It is important to mention that for such a reaction to take place C=O bonds should be formed during oxidation in preference to C—OH bond. This is what exactly happens has been shown by Manocha [16]. Figure 7 gives the infra-red spectrum of oxidized PAN fibres with time of oxidation (taken from reference 16). Since after the elimination of water during the oxidizing stage, chemisorption of oxygen takes place leading to C=O formation, if the fibres oxidized at the chemisorption stage are carbonized oxygen comes out during carbonization as CO and CO<sub>2</sub> thus plucking away of the carbon atoms from the chain. This process leads to the lowering of the strength of carbonized fibres carbonized out of oxidized fibres at the chemisorption stage. For carbonized fibres carbonized out of oxidized fibres in the water vapour evolution stage strength increasing mechanism due to cross linking predominates. For carbonized fibres out of oxidized fibres in the chemisorption stage the strength decreasing mechanism predominates. Hence there exist an optimum in the strength of carbonized fibres carbonized out of oxidized fibres oxidized for optimum time. This method of arriving at the optimum time of oxidation is the basis of the recent thesis of Manocha [17], which not only describe the optimum time of oxidation for both homopolymers and copolymers for each temperature but also gives the optimum stretch during oxidation besides other factors.



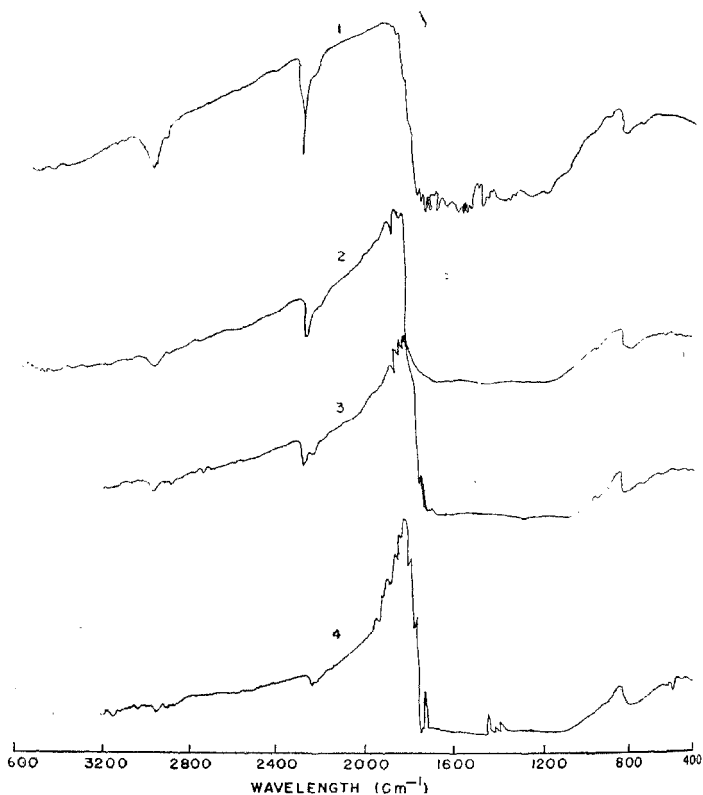


FIG. 7. Infra-red Spectra of Polyacrylonitrile fibres treated in presence of oxygen at 215°C for various times. (1) 100 mts., (2) 200 mts., (3) 300 mts., (4) 450 mts.

*Status of Carbon Fibres Development in India.*—National Physical Laboratory was the first Institution to develop carbon fibres. At present it has developed carbon fibres from imported PAN precursors from Courtaulds, U.K. getting a modulus of  $28 \times 10^6$  psi and a strength of  $250 \times 10^3$  psi going up to 1000°C alone [17]. However these Courtaulds precursors

are not available for sale. They are used purely in their own company for conversion into carbon fibres. We recently carbonized Japanese PAN precursors to get a modulus of  $25 \times 10^6$  psi and a strength of  $250 \times 10^3$  psi in a batch process going up to  $1000^\circ\text{C}$  alone. In a continuous process we are able to get a modulus of  $20 \times 10^6$  psi and a strength of  $180 \times 10^3$  psi. Japanese precursors are at least available for sale which costs about fifty rupees per kg in foreign exchange. It is very interesting to note that Iqbal Singh [18] carbonized indigenously available PAN precursors known of Jerkilon made by J and K Synthetic Ltd., India, by wetoxidation method. Going up to  $1200^\circ\text{C}$  alone he obtains a modulus of  $25 \times 10^6$  psi and a strength  $250 \times 10^3$  psi by batch process. This is the only report of carbonized fibres from indigenously made PAN precursors. The commercial availability of these indigenously PAN precursors which have been successfully tried for conversion into carbon fibres, will be made by 1979. IPCL, Baroda, is expected to make acrylic fibres in 1977. Every acrylic fibres made commercially is not suitable for conversion into carbon fibres unless they satisfy the conditions enumerated earlier. So we have to keep our fingers crossed until these precursors from IPCL are converted into carbon fibres. Central Leather Research Institute is now making PAN precursors which are still to be evaluated for conversion into carbon fibres.

NPL has made carbon fibres from Viscose Rayon [4] (Century Rayon) available indigenously. Going up to  $1000^\circ\text{C}$  alone we are able to get a modulus of  $6 \times 10^6$  psi and a strength of  $100 \times 10^3$  psi.

NPL has also made [19] carbon fibres from jute precursors for the first time in the World. Going up to  $1000^\circ\text{C}$  alone we get a modulus of  $5\text{--}6 \times 10^6$  psi and a strength of  $40 \times 10^3$  psi. However carbon fibres from jute precursors may not be viable since jute cannot be made into continuous fibres like regenerated cellulose called viscose rayon. Until this is done the work on carbon fibres from jute precursors will remain only as an academic interest. Gupta and Trehan have done TGA analysis of PAN precursors and oxidized PAN made in NPL [20].

*Carbon Fibres from Pitch Precursors*—Otani *et al.* [22] were the first to use PVC as starting material for carbon fibres. PVC was first converted into pitch by heating it in nitrogen atmosphere at  $400^\circ\text{C}$  when PVC turns into black pitch. This is extruded in the usual process, oxidized and carbonized and later on graphitized. The resulting modulus and strength are so low that they could not be used as they cannot be stretched at any stage except at graphitization temperatures. Otani [23] later on produced carbon

fibres from petroleum asphalt and these fibres are none the better as for strength and modulus are concerned. He describes the suitable material as characterized by the relatively high molecular weight and the large amount of and longer alkyl side chains. The special treatment required promotes the increase of aromaticity and the removal of low molecular components. The reason why these carbon fibres also have low strength and modulus is that they cannot be stretched except at the high temperature of graphitization namely 2500° C.

Recently Union Carbide, USA, has announced that they are able to obtain carbon fibres from pitch precursors to a strength of  $250 \times 10^8$  psi and a modulus of  $30 \times 10^6$  psi going up to 1000° C alone. This is very striking since so far only carbon fibres from PAN precursors have these properties. The starting material they claim is meso pitch.

Brooks and Taylor [24] were the first to explain the formation of meso-pitch when pitches either of coal tar or from petroleum base are heated in an inert atmosphere. The hydrocarbons present in the pitch first break and then recondense into bigger sizes. Thus with raising temperature spheres appear in the pitch-like mass and they grow further by coalescence. This is known as meso pitch. The insoluble particles like free carbon in the pitch are the nucleating centres for the growth of the particle. The same insoluble particles are the hindrance in coalescence. Thus the insoluble particles present should be small enough to nucleate the condensation of aromatic molecules but not large enough to prevent coalescence which leads to bigger sizes of condensed aromatic molecules. Therefore there exist an optimum concentration of insoluble particles in the pitches. Petroleum pitches were found to be more suitable as they contain less free carbon content as compared to coal tar pitches. Even among petroleum pitches the one having an optimum insoluble content will be a better precursor for having bigger sizes of meso pitch. Meso pitch of even 100 microns size has been obtained. Walker [25] reports that at about fifty per cent particles of meso pitch they begin to coalize and the formation of mosaic structure results. In individual mesophase spheres the platelets or flat aromatic molecules are aligned so that the edges of the platelets intersect the surface of the sphere at right angles. This is just what happens in delayed cokes, as contrasted to fluid cokes which are not graphitizable due to the onion-type structure of these fluids cokes. Walker [25] further argues that the main effect of the solids is that they reside at the surface of mesophase particles and thus binder the orderly coalescence of these particles producing well aligned a large mosaic regions. This further supports the

present thinking that mesophase spheres are a type of organic liquid crystal. That is their formation is a result of three factors (1) the increasing presence of aromatic molecules of large size, (2) increasing mobility of planer molecules with increasing temperature permitting the possibility of alignment and (3) an increasing probability of alignment as the planer molecules increase in size and hence Van der Waals attraction. It is these properties which make these meso pitch precursors to stretch and orient themselves in the direction of fibre at the spinning stage itself. This forms the patent of S.nger [26] which in turn form the basis of union carbide fibres made from meso pitch precursors. He takes the pyridine insoluble portion of pitch as mesophase. He concludes that if the meso pitch is to be spinnable it should not be thixotropic. Gopal Bhatia [21] in NPL has made meso-pitch of 45% concentration so far. He measures all the rheological properties of this mesophase pitch including thixotropy. Figure 8 gives the photograph of meso pitch obtained in NPL.

To sum up there exist to-day only three precursors which are capable of giving carbon fibres of reasonable strength and modulus. Table I gives the relative merits of these precursors.

It should be comparable to PAN precursors. Remembering the economic insuitability of hot stretched fibre at 2500° C it is only PAN and meso pitch precursors which are competitive. Out of these two, meso pitch precursors are better for low cost. But it still remains to be seen whether they form good composites. For certain use if impeller vanes in pumps used in fertilizer industry a low modulus and low strength carbon fibres do not preclude its use, for in this use only corrosive properties are important. One can use chopped fibres also in the composites in these cases. Even jute precursors (since chopped fibres can be used) are good enough for these purposes. The use of carbon fibres composites in fertilizer pumps can be very saving as it will replace costly metal alloys which are used at present. Satya [27] has actually used carbon fibres in composites which were tried for the impeller vanes in pumps of fertilizer industry in India. Here is a case where only carbon fibres can be used.

Another case where low modulus low strength carbon fibres can be used is in a cloth form for ablative purposes where thermal shock resistance is an important property which depends on low thermal expansion and high thermal conductivity. Herein even jute precursors can be used. Mukerjee [28] made carbon cloth from jute precursors using phenolic resins as matrix and these were successfully tried at Space Center, Thumba.

TABLE I

Precursor	Stretching behaviour	At 1000°C		At 2500°C		Stretching at 2500°C	
		Modulus $\times 10^{-6}$ psi	Strength $\times 10^{-3}$ psi	Modulus $\times 10^{-3}$ psi	Strength $\times 10^{-3}$ psi	Modulus $\times 10^{-3}$ psi	Strength $\times 10^{-3}$ psi
1. Viscose rayon	Can be stretched only at 2500°C	6	100	10	80	Upto 80 for 400% stretch	120
2. Polyacrylonitrile	Can be stretched at the oxidation stage itself (about 200°C)	30	300	60	250	80 to 10% stretch	300
3. Meso Pitch	Can be stretched at spinning stage	30	300	..	..	..	..



Fig. 8. Meso pitch of 20-30 microns size of 45% concentration.

In other fields there are two important spheres where carbon fibres are used. One is the use in day-to-day living the other is in defence and space. Glass fibres resin forced plastics are the common household name today. But these can be used for small size articles. But if want to build bigger sizes like big silos for open air storage in villages; large pipes of diameter 10 feet and above, large fishing boats of 120 feet length, large storage facilities for food and fertilizers, we have to use high modulus reinforcement to sustain large shapes. Glass fibres have at first a modulus of  $12 \times 10^6$  psi. Hence a hybrid of 50% glass fibres and 50% carbon fibres are suitable as reinforcement for these purposes. The carbon fibres should have at least a modulus of  $30 \times 10^6$  psi and a strength of at least  $200 \times 10^6$  psi for these purposes. At present only PAN and meso pitch precursors give carbon fibres of these requisite properties going up to  $1000^\circ\text{C}$  alone. For space use and aircraft use we must have light and strong fibres having a high modulus for reinforcement. Here only carbon fibres are suitable and a value of modulus  $60 \times 10^6$  psi and a strength of  $300 \times 10^3$  psi has to be the requisite property for these uses. Even here graphite fibres from PAN and meso pitch precursors are only suitable in the present knowledge. Cost of carbon fibres from meso pitch will be cheaper and these fibres will capture the world market in future. Further the cost of a material is related to the amount of production. For a price of carbon fibres of  $30 \times 10^6$  psi modulus and  $250 \times 10^3$  psi strength from PAN precursors to be of the order of 200 rupees per kg. It was calculated [29] that a minimum of

1000 tons per annum has to be produced. This production could not be made in UK and hence the price was prohibitively high in the 1960, which made Roles Royce Establishment which made these fibres almost close down at that time until the use is further advanced like golf clubs, etc. It is once again coming to life. Most of the uses of carbon fibres in USA is in golf clubs and fishing gadgets. In India the use to which carbon fibres can be put which do not exist in developed countries, are the ones mentioned earlier. Hence the consumption in India can be made to 1000 tons per annum thus making the cost competitive of being non corrosive and having a higher modulus. Recently in aircraft parts a mixture of Kevlar fibres and graphite fibre are coming into use [30]. So whether it is used in combination of glass fibres or in Kevlar fibre, carbon fibres have come to stay and in a decade from now carbon fibre composites will be as much as household name as glass fibre reinforced plastics at present.

*Carbon Composites.*—Epoxy resins is the versatile thermosetting resin which is used as matrix for carbon fibre reinforcement. However these composites can be used up to 135° C alone. This matrix gives good adhesion to carbon fibres. Phenolic resins are used mainly for ablative purposes because they will char under the application of intense heat to yield a high carbon content. Engelike *et al.* [31] have reported mechanical properties of Warmes 4028 phenolic carbon fibre material and have given the thermal conductivity heat capacity and useful temperature ranges for phenolic carbon fibre composites. In these applications one can use even low modulus carbon fibres. Polyimides can be used for higher temperature up to 350° C. Browning and Marshall [32] of the US Air Force Materials laboratory made carbon fibre, polyimide composites. Their composites gave flexural strength of about  $100 \times 10^3$  psi and interlaminar shear strength of about 5000 psi. They report that the loss in mechanical properties was very small up to 315° C. They conclude that carbon fibre polyimide composites can be fabricated having a low void content with 50% by volume fibre content and having mechanical properties comparable to those of epoxy resin composites at room temperature but much better at elevated temperature. Most recently a comprehensive study of carbon fibre reinforced polyimides has been given by Heym [33].

Thermoplastic resins like Nylon 6, 6, 6, 6, 10, 6-11 and 6-12 are also used as matrices for reinforcement of carbon fibres. But these thermoplastic materials do not wet carbon fibres. Hence most of the effort has been centered upon using chopped fibre which may be intimately premixed with the plastic matrix. In such a system the strength and modulus of

the composite are found to be low. But if one uses pultrusion technique for these composites with chopped carbon fibres, one can align these fibres in the direction of pultrusion and hence can get increase strength and modulus in the direction of pultrusion. These thermoplastic resins can best be used however for carbon fibres composites in friction and wear applications. Lancaster [34] has done extensive work in this direction.

Carbon fibre metal composites are of recent origin. A noteworthy advantage of metals is their high temperature capability when compared with even the most advanced resins. However chemical reaction between carbon and the metallic matrix must be inhibited by Barriers [35].

Dononan and Watson Adams [36] describes the use of electro deposited nickel in carbon fibre composites. Nickel alloys are traditionally used for all kinds of high temperature applications. One use of carbon fibre nickel composites is high temperature blades for aircraft engines, as distinct from carbon resin blades which have been used at relatively low temperatures at the front end of the air compressors.

Aluminium matrix has applications when combined with carbon fibre. One potential use is for electricity transmission lines, the aluminium carrying the bulk of the current while the fibres provide high tensile strength allowing greater distances between transmission towers.

There are various other matrices which can be used for reinforcement of carbon fibres. Some examples are rubber and ceramics. These composites as well as the use of carbon fibre composites in various fields are optly described by Gill [37].

In metal composites as well as composites with thermoplastics the main problem is the wettability of carbon to these matrices. Aggour and Fitzer [38] describe a method to overcome this difficulty. The method consists of depositing SiC on carbon fibres by chemical vapour deposition by passing methyl-chlorosilanes in nitrogen and hydrogen atmosphere. This deposition not only makes the deposited carbon fibres to be adhesive to matrix, it also protects the carbon fibres from oxidation. One factor which seem to have been forgotten is the ability of the matrix molecules to enter the pores of fillers in order to get good locking behaviour. Carbon fibres being smooth may not have surface pores sufficient enough to admit a matrix molecule specially that of metals and thermoplastics and this may be the reason for bad wetting. Petroleum coke particles have excellent



wetting with pitch binders which are thermoplastic. It is because these coke particles have innumerable pores on the surface which can admit the binder molecule and give a good locking behaviour. But graphite particles especially natural graphite do not wet as much as petroleum coke with pitch binders because of the fact they are smooth plate-like surfaces with pores on surface not big enough to admit binder molecules. Therefore the reason for carbon fibres not wetting either thermoplastic or metals must be in its smooth surface with surface pores small enough so as not to admit the matrix molecules. Graphite fibres do not wet enough epoxy matrices because of their smoothness. Graphite fibres are specially treated by either ion bombardment or oxidative treatment thus creating etch pits on the surface to improve their adhesion to matrix. The edge pits created should be sufficient to admit the resin molecule but not more as to reduce the strength. Hence there exist optimum level of etch pits which can be created by the above treatment. If the graphite particles are rough enough to have surface pores sufficient to admit the matrix then they can well adhere. Rohtagi [39] was able to disperse fine particles of graphite in aluminium which give good wetting. It is very important then to determine the cluster size of metals and then compare it with the actual pore created on fibre surface to understand the wetting behaviour. This gives entirely another approach for the wetting of carbon fibres to matrices. The last but not the least in understanding the composite behaviour is to study the complexes formed on carbon fibres which do play a role in wetting.

#### CHARACTERIZATION

*Strength and Modulus.*—Johnson and Tyson [40] were the first to study the variation of strength of carbon fibres with temperature and correlate this variation with pore size development with X-ray low angle scattering. Figure 9 gives this variation.

The Young's modulus varies as  $l_p$  (known as parod's distance in low angle X-ray scattering terminology). The explanation given by the author is that at the lower temperature below  $1000^\circ\text{C}$  where carbonization is taking place  $l_p$  and  $l_c$  (crystallite length) are small so that in effect the fibres contain a large number of small pores which can just be distinguished in high resolution electron microscope images. Consequently there is a greater possibility of cross linking between the small crystallites involving crystallite edge atoms and interstitial atoms which at this temperature could be residual N atoms. After  $1000^\circ\text{C}$  the pore size increase further and at the graphitization stage around  $1900^\circ\text{C}$  there exist small number of larger

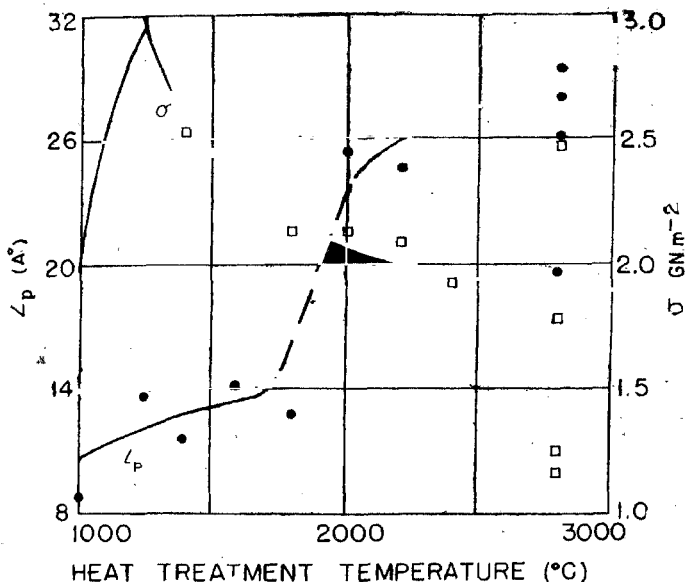


FIG. 9. Low angle parameter and ultimate tensile strength plotted against temperature of graphitization for a range of carbon fibres. □ are values of  $\sigma$  and ● are  $L_p$  values.

pores. At this stage the cross linking breaks allowing the chain length at different heights to rotate and align themselves in the basal plane thus giving rise to three-dimensional graphitic structure. Due to the breakage of cross links strength falls. This picture is not only true of carbon fibres but also for all carbon artifacts. Only difference in the case of large carbon artifacts the pores responsible are bigger in size as to be resolved by mercury porosimetry.

While the decrease of strength and increase of modulus after the strength reaches maximum is understandable, the increase of modulus with strength in the lower ranges is not clear by the above argument. Since modulus is only dependent on the orientation of crystallites only mechanism which can account for orientation in the lower temperature ranges is suitable. Here we can think of pores getting elongated in the direction

of fibre and shortened in the direction along the diameter as more and more shrinkage takes place in the diameter as temperature proceeds. Since the crystallites have to bend over the pores, this explains greater orientation of crystallites as the pores get more elongated in the fibre direction. Hence modulus increases. The same explanation will hold good in the case of hot stretched fibres where both strength and modulus increase with temperature even after  $1900^{\circ}\text{C}$ . The only difference is the pores elongate in this case in the direction of fibres length due to stretching as contrasted with that in the earlier stage of temperature, due to shrinkage in diameter. This can be proved by actually observing pore shape as carbonization temperature increases. As they get shortened in the diameter direction and elongated in the direction of fibres, the pores get more ink-bottle-shape as exist in coal. The experimental difficulty in determining the shape of the pore poses a formidable problem. While the scanning electron microscopy can only detect a pore on a surface to about  $1000^{\circ}\text{A}$  depth, it cannot detect a pore at the centre of fibre say 3 to 4 microns from the end. While we can go on etching the surface until we come to the centre and take the scanning microscope picture, this procedure itself creates more pores than which already exist. Hence there is no way except to construct the model of the shape by the study of both physical adsorption with different molecules and X-ray low angle scattering. The X-ray low angle scattering gives the largest distance of the pore in the diameter direction. Figure 10 gives the X-ray low angle scattering of PAN carbon fibres taken by Kundra [41]. The sharp intensity profile shows that the pore length is



FIG. 10. X-ray low angle scattering of PAN fibres carbonized to  $1000^{\circ}\text{C}$ .

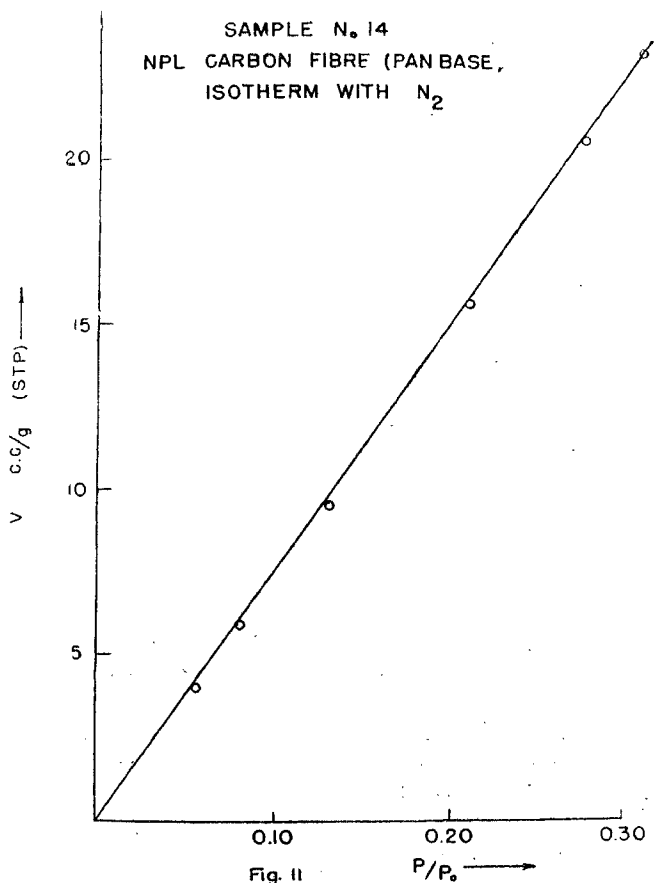


FIG. 11. Absorption isotherm of PAN fibres carbonized to 1000°C.

oriented in the direction of fibres. Physical adsorption data gives the pore opening combined with the surface area which ought to be the same from both physical adsorption and X-ray low angle scattering one can

construct model of the pore shape. This is the only method available while X-ray low scattering presents no difficulty, the physical adsorption in carbon fibres presents great difficulty. The very isotherm from which adsorption results can be computed is entirely different for carbon fibres different from the usual isotherm from which one can get pore size and surface area from the BET equation. Figure 11 shows the isotherm obtained by Bohra [42]. Instead of the usual concave curve to the pressure axis you get a straight line. The interpretation of such an isotherm is still awaited. Unless this is solved we cannot determine the pore mouth diameter and the whole experimental determination of shape of pore becomes difficult. Here is a field of challenging experimental possibilities which has not been solved until now.

While this is the situation of strength *versus* temperature presented by Johnson [40], Moreton and Watt [43] present the variation of strength with temperature for carbon fibres prepared from precursors spun in clean room conditions. Figure 12 presents their data. They explain that impurities in the PAN precursor were the major cause of flaws in carbon fibres. Fracture was usually found to start either at surface flaws at voids formed by the volatilization of inclusions during processing. Contamination by impurity particles can occur at any stage of the carbon fibre process. Thus inclusions may be present in the PAN spinning solution or surface impurity may be picked up either during spinning and collection or during subsequent bandling and conversion to carbon fibre under normal laboratory conditions surface contaminations cannot be avoided. Figure 12 shows that carbon fibres made under clean room conditions have not only greater strength compared to controlled ones, they also show increasing strength with temperature throughout. The decrease in strength after 1000°C for controlled ones is attributed to melting of surface particles creating a void. This explanation shows that the strength reduction is due to surface flaws alone. However voids in the interior also play a part. Stress concentration are created at the void surface and these will initiate cracks and these cracks propagating across the fibre may create catastrophic breaking. On the other hand even though cracks are initiated, they may be prevented from propagating, thus containing the cracks locally. It is the interplay of these two factors namely initiation and propagation of cracks which will determine ultimately the strength of fibres. There is still lot of scope for further work in this field.

*Electronic Properties.*—The most exhaustive work on the electronic properties was done by Robson *et al.* [44]. They observe that the  $g$  value

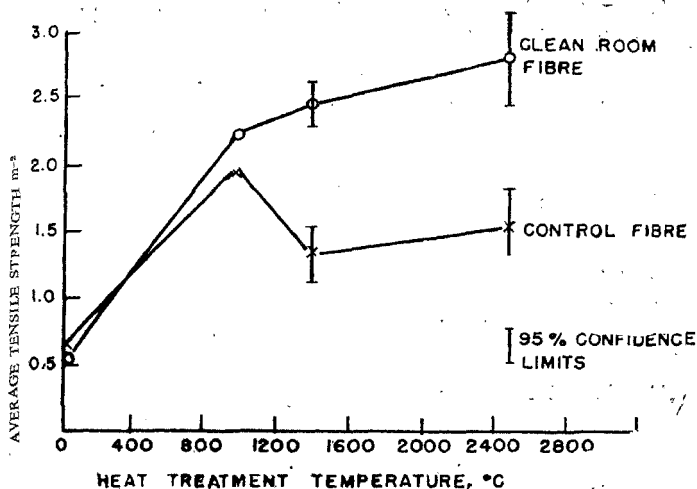


Fig. 12. Effect of heat treatment temperature on fibre strength.

in electron spin resonance exhibits anisotropy in the vicinity of temperature around  $1750^{\circ}C$ . The appearance of this anisotropy was associated with discontinuities in other electronic properties.

*Measurement of Longitudinal Resistivity.*—The single carbon fibre was stretched under light tension on a microscope slide—electrical contacts were pointed on the fibre and its resistance was measured by means of a standard four probe technique using a sensitive potentiometer. It was noted that the resistivity of carbon fibres was lower than that for graphitizing carbons, except for higher heat temperature. This finding is contrary to the usual fact that graphitizing carbons are always having lower resistivity than for carbons treated at lower temperatures. Examination of the behaviour of the resistivity with temperature reveals that between  $77^{\circ}K$  and  $300^{\circ}K$  it decreases more or less linearly with increasing temperature. Because of this non-linear relationship  $\rho_{77K}/\rho_{300K}$  known as resistivity ratio can be taken as a measure of the temperature dependence of these materials. This resistivity ratio reaches a minimum value of about  $1750^{\circ}C$ .

*Thermo Electric Power.*—The variation of seebeck coefficient with temperature shows that at lower heat treatment temperature up to about 1500°C, the seebeck coefficient more or less follows that for soft carbons but at a higher HTT it appears to level off at a value which is lower than that attained by soft carbons without going to the maximum, as happens with soft carbons at about 2000°C. This behaviour is clearly in line with the nominally non-graphitizing nature of the carbon fibres. It is again interesting to note that the seebeck coefficient of these fibres changes sign at a HTT of approximately 1750°C.

*Magneto Resistance.*—The field dependence of the transverse magneto resistance was investigated for fibres at three different temperatures 4.2°K, 77°K and 300°K. The variation of the magneto resistance with HTT at these temperatures is shown in Fig. 13. The magneto resistance becomes negative at about 1750°C.

Toyoda and Mrozowski [45] reporting on the electronic properties of soft carbons have come to the conclusion that although the behaviour of samples heat treated above 2000°C generally substantiated the two band model, those treated below about 1800°C were anomalies and the presence of radically different band structure appeared to be indicated. A positive hole conduction process as postulated in Mrozowski's band model, requires positive thermo electric power. The negative seebeck coefficients which were observed by Robson *et al.* [44] between about 900°C and 1750°C have therefore been rather anomalous. This discrepancy has not yet been cleared at present. Again the appearance of positive magneto resistance below 1750°C could not be explained by any model so far. Perhaps here as suggested by Robson [44] we have to look for these discrepancies in terms of Mott's model [46] which gives the band theory of disordered lattices. Here is challenging field of research which is still to be explored.

## CONCLUSIONS

Attempt has been made in this article to review the status of carbon fibre development. Instead of reviewing all possible carbon fibres developed attention has been focussed mainly on carbon fibres based on PAN precursors which is the current fibres with requisite modulus and strength. However the future will see the outcome of carbon fibres based on meso pitch precursors. The characterization which has been cited in this review will be equally applicable for all carbon fibres based on different precursors.

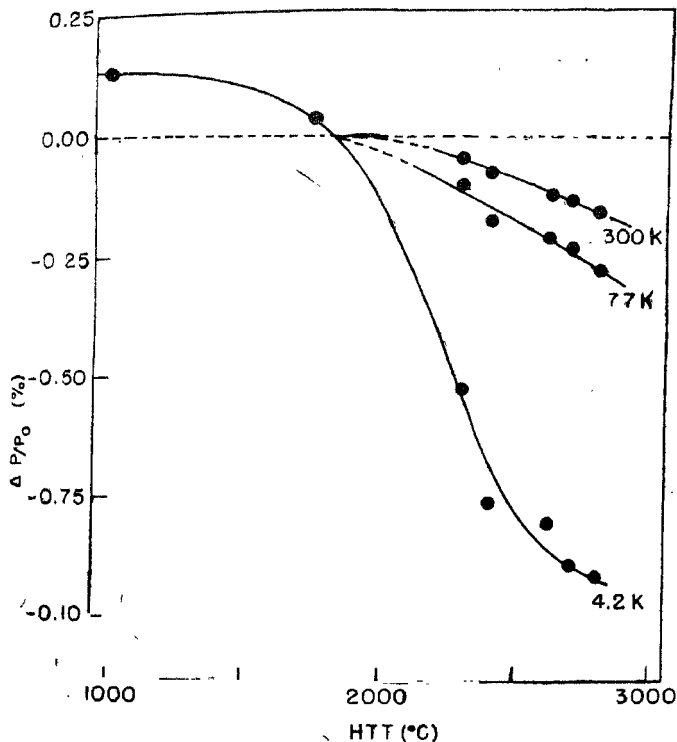


Fig. 13. Variation of a transverse magneto resistance with processing temperature at a field of 14.1 G.

Some of the unexplored research work has been indicated. In the field of characterization still lot remains to be done which will give us a better understanding of the nature or carbon fibres. This will in turn make us realize greater potentialities of carbon fibres from the existing precursors.

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