

## Carbon Fibres\*

M. SANTAPPA

University of Madras, Madras-600 005

1. The improvement in mechanical properties of materials has been generally centered on strength. With isotropic materials like many metals only strength can be improved; on the other hand with anisotropic materials like graphite and organic polymers both strength and modulus can be varied by changing preferred orientation. With depletion of natural mineral sources it is necessary to develop suitable alternative materials for various structural applications essentially to replace metals. The strength and modulus of graphite has made it a suitable substitute for structural materials with the attendant advantage of light weight.

### 1.1 Carbon and Graphite

The chemists and technologists, therefore, have tried various precursor materials for the production of carbon or graphite essentially for high temperature reactors, gas turbines, high speed aerospace vehicles, etc. The predominant factor holding further development is the limitation imposed by the mechanical and physical properties of currently available materials particularly for use at high temperatures<sup>1</sup>. The refractory nature and chemical inertness of carbon has proved valuable in applications such as insulators, packing materials, catalyst supports, electrical heating elements for special environments etc. In recent years an entirely new use has emerged for carbon fibres as an ablative material to resist very high temperatures developed on re-entry of space vehicles into the earth's atmosphere.

### 1.2 Composites

The most recent use for the carbon fibre reinforced plastics (CFRP) or even metals is in the preparation of composites of exceptionally high specific stiffness and strength. The basic concept of fibre reinforcement<sup>2</sup> is the production of a two phase composite structure in which deformation of the matrix is used to transfer stresses by means of shear tractions at the fibre matrix interface to the embedded high strength fibres. Provided the length of the fibre is sufficient, the latter should then be constrained to take up the same deformation as the matrix over the greater part of their length and thus effectively reinforce matrix. Carbon or graphite fibre reinforced composites provide an equivalent stiffness to steel for only one-fifth of the mass and twice the stiffness of aluminium for only half the mass. With these properties, carbon fibre reinforced plastics find extensive applications in

various vital fields such as aerospace, agriculture, sports engineering, medicine etc.

### 2. Precursors for Carbon Fibres

2.1 The pyrolytic decomposition of organic polymers provides a useful method of preparing special types and physical forms of carbon. In many cases the shape or physical form of the organic precursor is retained during high temperature treatment or carbonisation. This principle has been applied extensively in the preparation of carbon fibres from fibres of cellulose, rayon, polyacrylonitrile and other polymeric materials. In general, the suitability of materials for the production of carbon fibres should satisfy the following basic requirements:

- The fibrous form should be retained on pyrolysis, i.e. the material must not melt or deform when heated,
- The carbon skeleton should be capable of being readily changed into two dimensional graphite structure, and
- The pyrolysis should take place without appreciable loss of volatile carbon compounds.

These requirements are satisfied by cellulose<sup>3</sup> and cross-linkable polymers such as polyacrylonitrile (PAN). The reason<sup>4</sup> for their high melting temperatures is that relatively strong intermolecular forces inhibit molecular motion. However, the cause of these forces are different in the two polymers—PAN and cellulose. In PAN, highly polar cyanide groups cause strong dipole-dipole forces to operate between molecules, whereas in cellulose the repeat unit,  $\beta$ D-(+)-glucose unit, is a trihydric alcohol, so that the intermolecular forces result from hydrogen bonding interactions between hydroxyl groups and adjacent molecular chains.

The other potential candidate with promising prospects, both in price as well as in performance, are the pitch fibres. The pitch fibres are melt spun from Mesophase pitch derived from several sources like 'coal tar', 'PVC' pitch and 'coal'. Mesophase pitch is nothing but the liquid crystal state of pitch heated to temperatures above 350°. It is then melt spun, thermoset and carbonised at temperatures of 1500-3000°C.<sup>5,6</sup>

The other polymeric precursor materials include lignin<sup>7</sup>, polyvinyl alcohol<sup>8</sup>, *p*-polypropylene<sup>9</sup>, polyphenylene<sup>10</sup>, phenol hexamine thermoset resin and a cured novolac phenolic resin<sup>11</sup>, polyimides<sup>12</sup>, pitch

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of polyvinyl chloride<sup>18</sup> etc. Attempts are also being reported for making carbon fibre directly from hydrocarbons<sup>14</sup>.

Although these high performance and speciality fibres are called by the generic term carbon fibres, two types of such "carbon and graphite fibres", depending on the heat treatment temperatures have been identified:

**Type I. Carbon fibre, 'High Modulus'** Well defined graphite structure with 99.9% carbon content is obtained when fibres are heated to 2000°. (Tensile strength 200-300  $\times 10^6$  psi; Youngs modulus: 55-60  $\times 10^6$  psi).

**Type II. Carbon fibre, 'High-Strength'** The graphite crystals which are not well defined and with 90-98% carbon content are formed when fibres are heat treated to 1200°. (Tensile strength 350-450  $\times 10^6$  psi; Youngs modulus: 35-40  $\times 10^6$  psi).

At high temperatures the order of graphitization in carbon layers increases and approaches ideal graphite structure. The layers glide down and the strength decreases.

## 2.2. Cellulose

The first successful material used for the production of carbon fibres is cellulose in its original form as well as in the regenerated form. It was Edison (1880) who developed carbon filaments from cellulose for incandescent lamps. The finite length of cellulose in its native form has led to the development of regenerated cellulose or rayon with improved physical and mechanical properties<sup>19-21</sup>.

Tang and Bacon<sup>19</sup> carried out much useful work in the carbonisation of cellulose precursors. They proposed a multistage mechanism for the conversion of cellulose to carbon. The fibre undergoes physical and chemical changes during the heating cycle from 100° to the final stage of carbonization; 700° to 1000°.

### (a) Pyrolysis: oxidation:

- Stage (i). Physical desorption of water (25-150°).
- Stage (ii). Dehydration from adjacent H and OH groups of cellulose unit (150-240°).
- Stage (iii). Thermal cleavage of the cyclic linkage and scission of C-O bonds and some C-C bonds via free radical reactions (240-400°) leading to formation of C, CO and CO<sub>2</sub>, etc.
- Stage (iv). Aromatisation at above 400° and formation of fused ring or ladder structures.

(b) Carbonization and graphitization. After pyrolysis the fibres are carbonized upto 1000° under tension<sup>22-24</sup>. The tension is to be increased for higher temperature, 2750°, so that an extension of 30% takes place<sup>24</sup> and fibres with modulus of 50  $\times 10^6$  psi are obtained.

Disadvantages of this process are:

- (i). It gives a low carbonization; low yield of carbon fibre and takes long time for this. The theoretical weight loss in the process of carbonization is 55%; but in practice the weight losses are 70-90%.
- (ii). The cross-section is not of a regular shape but zig zag<sup>25</sup>.
- (iii). Stretching at high temperatures at 2250° involves high energy requirement and therefore uneconomical.

The development of carbon fibres from polyacrylonitrile fibres at low temperatures has led to replacement of carbon fibres from cellulose.

## 2.3. Polyacrylonitrile (PAN)

2.3.1. One of the most successful precursor materials for manufacturing high modulus and high orientation carbon fibres is PAN. It has an all-carbon backbone and gives greater yields of carbon than cellulose. It stabilises when heated to 200-220° in oxygen. The chemistry of the reactions in PAN pyrolysis are well studied and documented<sup>26-28</sup>.

2.3.2. Use of comonomers: Most commercial PAN fibre precursors for carbon fibres contain comonomers, such as methyl acrylate (the most widely used), methyl methacrylate and vinyl acetate etc. These are copolymerized with acrylonitrile to increase the solubility of the co-polymer in various solvents such as DMF, DMAC, nitric acid etc. Small amounts of olefinic monomers are often included, usually along with a neutral monomer, to enhance dyeability. Although theoretically the strength and modulus of carbon fibres based on PAN homopolymer should be high, comonomers are used for ease of processing and solubility. This comonomer content is as high as 15% in the textile grade PAN while it is 6% for carbon fibres. Information is scanty regarding the effect of comonomers during the carbonization of PAN fibres. Fitzer and his co-workers<sup>29-32</sup> have found that the optimum comonomer content around 3% is beneficial for both tensile strength and modulus of C-fibres.

2.3.3. The processes: The steps that lead to graphitization of PAN fibres are (a) oxidation, (b) carbonization and (c) graphitization.

The fibres are given a stretch before they are oxidised and cyclised at 70-100°. The ring closure takes place at a temperature of 100-220° leading to thermally stable polymer. Next stage is carbonization in inert atmosphere from 300-700°. Condensation and cross-linking takes place with the elimination of hydrogen cyanide, ammonia and water and

formation of hexagonal, possibly aromatic, structures. Beyond 700° upto 1000° fibres still contain 7% of nitrogen and some hydrogen but the type of physical and chemical bonding is not known. At 1500° carbon fibres of high strength are formed.

Graphitization in inert atmosphere takes place at ~1800-3000° with the elimination of all the elements other than carbon. Molecular re-arrangements take place giving graphite crystal structure resulting in high modulus fibres.

(a) *Oxidation*: Examination of these stages in detail reveal the importance of oxidation step which is to convert the acrylic polymer into a thermally stable ladder polymer.

It does not undergo chain scission reactions when heated strongly. Chain scission and related molecular disorientation would have catastrophic effect on the texture of the resulting carbon fibres and hence on their mechanical properties.

The cyclisation by which the ladder polymer is formed is the first reaction to occur after the acrylic polymer is heated above its second order transition temperature. The increased molecular motion allows the adjacent cyanide groups to approach close enough for reaction to occur between them induced by their dipoles. The new bond is formed after the migration of an electron pair from cyanide triple bond. In view of an effectively greater negative charge on the nitrogen atom, further ring closure occurs with corresponding ease.

Grassie<sup>21</sup> postulated that cyclisation can also be initiated by the presence of an acidic group which may be incorporated as the dye site.

The most important types of reactions during thermal treatment of PAN are 'dehydrogenation' and 'cyclisation'. Many investigators suggested the course of reactions in which cyclisation precedes dehydrogenation. The other possibility is based on the assumption that especially in the presence of air dehydrogenation occurs prior to cyclisation. From the results of other authors it can be concluded that cyclisation and dehydrogenation occur simultaneously. Fitzer and Muller<sup>22</sup> from the IR and DTA measurements favour the combined mechanism with dehydrogenation preceding cyclisation. They conclude that at the end of cyclisation the dehydrogenation is not complete.

Watt and Johnson<sup>23</sup> oxidised two sets of fibres — one, terpolymer with 95, 4.6 and 0.4 mol % of acrylonitrile, methyl acrylate and vinyl acrylic compound (vinyl acrylic compound is added to act as a dye site); the other, a copolymer with 95.4 and 4.6% of acrylonitrile and methyl acrylate. When they were oxidised as such the oxygen uptake with time was very poor in the case of the second without acidic comonomer as compared to the first with acidic comonomer. When they were vacuum preheated and then oxidised, the first one did not show any improvement on oxidation with regard to oxygen uptake whereas the second copolymer showed a marked increase in the oxygen

uptake. These clearly show that the carboxyl containing group definitely plays a key role in aiding cyclisation. These results are seen in terms of oxygen uptake with oxidation in air at 230° when Courtelle and Orlon fibres are compared. When they are vacuum pre-heated and then oxidised, Courtelle fibre did not show much difference in oxygen uptake but Orlon did. This shows that in the Courtelle fibre the oxidation, the cyclisation and ladder structure formations are aided by the carboxyl comonomers during vacuum preheating stage.

The oxidation step is a very important one as it produces an oxidized polymer structure approximately parallel to the fibre axis which may be regarded as a template for the formation of oriented carbon fibre.

To obtain quality material it is necessary to control this polymerization through oxidation and stabilization<sup>24,25</sup>.

Chemical reactions involved during oxidation are:

- (i). initiation of nitrile polymerization,
- (ii). propagation of nitrile polymerization,
- (iii). oxygen uptake,
- (iv). dehydrogenation, and
- (v). minor loss of volatile materials.

The exact structure of this oxidised polymer is not clear although lot of work has been carried out. The infrared spectrum<sup>26</sup> shows the disappearance of  $-C \equiv N-$  and formation of  $-C=N-C=N-$  conjugated double bonds. The differential thermal analysis shows decreased exotherm with the formation of partially oxidised films indicating that the stabilization is achieved by oxidation and cyclization.

The significant contribution is due to Shindo<sup>27</sup> who thought that oxidation preceded carbonization. Watt, Philips and Johnson<sup>28</sup> introduced the concept of holding the fibre under controlled tension during the oxidation stage. This meant the necessity to maintain alignment of the original polymer molecules prior to carbonization, and therefore attainment of truly high strength, high modulus fibres during oxidation itself without the need for stretching during graphitization stage.

(b) *Carbonization*: After oxidation the fibre is slightly reduced in diameter and becomes black. Fibres are carbonized under load (tension) over many hours to 1500° to drive off most elements other than carbon. The small molecules like  $NH_3$ , HCN and  $H_2O$  are removed and high strength fibres result.

(c) *Graphitization*: For type I carbon fibres the graphitization temperature is usually from 1800 to 3000° in the presence of argon. There is an increase in the preferred orientation of the crystallites with increasing graphitization temperature which accounts for the increased motion.

In order to improve the strength and modulus of carbon fibres Moreton and Watt<sup>38</sup> carried out spinning of PAN fibres under clean room conditions in order to minimise the impurities which deter the carbon fibre properties. They stipulated the clean room condition to less than 100 particles/ft<sup>3</sup> which could be achieved using laminar flow filters above the spinning zone. Johnson and Thorne<sup>39</sup> have investigated the fracture surface of carbon fibres with SEM and concluded that impurities in the PAN precursor were the main cause of flaws in carbon fibre.

Some interesting research findings have been reported recently<sup>40</sup> revealing the production of carbon fibres from PAN at low temperatures such as 600-900°. In the process it is described that the resulting carbon fibres possess strength with nearly twice the tensile strength as compared to the old process in that temperature range. The process consists of giving PAN fibres a pre-treatment with molten benzoic acid at 175° and acetylene prior to the oxidation step. This is referred to as 'modified process'. Exhaustive fundamental work has to be done before it could take a firm standing to replace the old method.

A good amount of fundamental work on the aspects of oxidation, carbonization and graphitization are reported<sup>41-46</sup>. The structure of PAN fibre is due to Bennett and Johnson<sup>46</sup>.

The work of Rolls Royce highlighted a number of important aspects associated with the heat treatment stages.

THE FORMATION OF CARBON FIBRE: SEQUENCE OF EVENTS THROUGH HEAT TREATMENT

Process	Temperature	Event
Oxidation in air	70-100°	Molecular relaxation at glass transition temperature prevented by securing fibres to rigid frame.
	160-220°	Oxidation and oxidation reaction leading to thermally stable ladder polymer.
Carbonization in inert atmosphere	800-1000°	Condensation and cross-linking reactions with the elimination of hydrogen cyanide, ammonia and water, and the formation of hexagonal, possibly aromatic structures.
	1000°	Fibres still contain 7% nitrogen and some hydrogen but the type of physical/chemical bonding is not known.
	1600°	Carbon fibre type II.
Graphitization in inert atmosphere	1800-3000°	Elimination of all elements other than carbon.
		Molecular re-arrangement giving graphite crystal structure. Carbon fibre type I.

#### 2.4. Other precursors for carbon fibres

The search for a precursor that is cheap in cost and abundant in availability has been the requirement for carbon fibres in numerous applications. Because of these considerations it provided impetus

to work on pitch based carbon fibres. The work on pitch fibres was started in Japan<sup>47-49</sup> where carbon fibres of low modulus and strength were produced at earlier stages. Union Carbide has produced pitch based carbon fibres which appear to pose as a competitor for the PAN based one. However, it will take few more years for the pitch based precursor to become a potential competitor for PAN fibres.

PVC was one of the first starting material for the pitch based carbon fibres. Ohtani<sup>49</sup> produced pitch from PVC by heating the latter in nitrogen atmosphere at 400° for 30 min. The carbon fibres were melt spun from pitch which softened at 150° and turned into viscous liquid at 200°. Apart from PVC<sup>49</sup>, coal tar<sup>50</sup> and coal<sup>51</sup> are used as starting materials for pitch based carbon fibres.

The Union Carbide improved the position of pitch based carbon fibres by introducing a process wherein coal tar pitch is made use of instead of the PVC pitch. In this process coal tar pitch is heated to a stage of converting pitch partly to a liquid crystal or mesophase state which occurs during pyrolysis between 350-500°. From the mesophase, the fibres are melt spun and carbonized and graphitized subsequently. The structure of mesophase from electron micrographs (the EM pictures of the anisotropic mesophases formed in isotropic petrol pitch by that treatment at 400°) and the model of the liquid crystal mesophase which consists of planar polyaromatic molecules<sup>52</sup> are interesting. Mesophase spherules are formed by orientation of poly condensed aromatic hydrocarbons along lamellae and by accumulation in layers. As they already have high order in the mesophase stage, when drawn in such a stage the fibres possess high Young's modulus.

Union Carbide has placed in the market TFC-mel type P, Thorne I 50 and Thorne I 300. There are several recent references that outline the carbon fibre production from coal through the process of solvolysis/liquefaction of coal. The production of coal involves milling and sieving it to a fine powder. It is extracted with benzene and the benzene insoluble portion is heated at a rate of 10°/min upto 450°. This contains 9% mesophase pitch. Refined pitch in its mesophase form is melt spun, oxidized, carbonized and graphitized to produce carbon fibres. The comparison between the PAN and pitch based carbon fibres show that the latter possess inferior tensile strength. However, the results reported by Bacon<sup>53</sup> recently, throw light on the improvement of strength comparable with PAN based carbon fibres by eliminating structural flaws. Cost wise, the carbon fibres from pitch show an edge over the PAN based carbon fibres—1 lb of high strength and high modulus carbon fibres from PAN cost \$35/lb to \$42/lb while that of carbon fibres from pitch of comparable strength and modulus cost only \$20/lb. With the increase in production the cost may well come down. The pitch fibres have an added advantage of having 80% of yield of carbon as compared with

PAN which has only 50% and hold good promise for future as precursors for carbon fibres.

The processes for manufacture of carbon fibres from the three precursors—cellulose, PAN and pitch are therefore very interesting.

### 2.5. Development of suitable precursors at CLRI

Acrylonitrile and its copolymers are found to be better precursors because of their unique property to form ladder type of structure and high carbon yield. In the textile grade PAN the comonomer content is high which is not advantageous for carbon fibres for composites<sup>22</sup>. The production of special grade PAN fibre is controlled by several international patents and is a closely guarded secret by the fibre manufacturers. Hence it is necessary to develop a suitable method for the development of acrylic copolymers with more than 90% acrylonitrile with various comonomers.

The presence of oxygen containing monomers in the copolymers of PAN facilitate oxidation and carbonization. Hence a variety of copolymers containing 3-15% comonomers were prepared:

- Polyacrylonitrile-co-methyl acrylate,
- Polyacrylonitrile-co-butyl acrylate,
- Polyacrylonitrile-co-vinyl pyrrolidone,
- Polyacrylonitrile-co-vinyl acetate,
- Polyacrylonitrile-co-methyl methacrylate.

Using laboratory devices these polymers were tested for their spinnability and carbonization characteristics and 'a' has been identified as a potential candidate.

## 3. Fibre spinning

3.1. The spinning of the PAN copolymers can be done by both wet and dry spinning processes. In the 'wet spinning' the copolymer is dissolved in a suitable solvent such as DMF, DMSO, DMAC or nitric acid and spun through the corresponding dilute solution of the solvent in water and subsequently subjected to washing and stretching. In the 'dry spinning' process, the copolymer is dissolved in solvents such as DMF or DMAC and hot air is blown through the fibres emerging from the spinnerette face to remove the solvents. The solidified fibres are then subjected to further stretching before being collected on frames. An improved form of wet spinning of acrylic fibres is to hold the spinnerette one cm above the coagulation bath. This method called 'dry jet wet spinning' produced more oriented and compact structure<sup>24</sup>.

Fundamental studies such as effect of coagulation bath temperature, molecular weight of the copolymer and additives on the mechanical properties of precursor (PAN fibre) have been carried out at CLRI besides spinning fibres for carbonization. The polymers made were characterized by GPC, viscosity, elemental analysis and X-ray diffraction methods and the spinning conditions were fixed for each polymer depending on the solubility and molecular weight using a mechanical spinning assembly (Fourné, West Germany).

### 3.2. Effect of coagulation bath temperature

The temperature of the coagulation bath was varied from 10 to 50 and the minimum fibre breakage and better mechanical properties were obtained<sup>26</sup> when the coagulation bath temperature was low.

EFFECT OF BATH TEMPERATURE ON PRECURSOR AND CARBON FIBRE

Sl. No.	Bath temp. °C	Stretch ratio	Precursor		Carbon fibre	
			T.B. × 10 <sup>3</sup> psi	M × 10 <sup>3</sup> psi	T.B. × 10 <sup>3</sup> psi	M × 10 <sup>3</sup> psi
1.	10	1:8	96	1.4	110	12
2.	20	1:8	76	0.9	95	14
3.	30	1:8	61	0.8	60	

### 3.3. Effect of molecular weight

Variation of polymer molecular weight and the consequent distribution by change of the polymerization temperature was studied. The polymers were analysed by viscosity and GPC. The GPC data clearly indicated the narrow molecular weight distribution for the low temperature polymer and spreading of molecular weight at higher temperature<sup>26</sup>. Effect of molecular weights on fibre properties is also very striking.

VISCOSITY AND GPC ANALYSIS OF THE POLYMERS PREPARED AT DIFFERENT TEMPERATURES

Sl. No.	Polymer	Viscosity	Elution volume
1.	P <sub>1</sub>	2.66	51
2.	P <sub>2</sub>	1.965	50, 58.5, 58
3.	P <sub>3</sub>	1.10	51, 55, 59
4.	P <sub>4</sub>	0.95	52, 56, 60.5

EFFECT OF MOLECULAR WEIGHT ON FIBRE PROPERTIES

Sl. No.	Polymer	Stretch ratio	Diameter	T.B. × 10 <sup>3</sup> psi	Modulus × 10 <sup>3</sup> (psi)
1.	P <sub>1</sub>	1:10	16	73	1.02
2.	P <sub>2</sub>	1:8	18	64	1.19
3.	P <sub>3</sub>	1:6	22	55	1.10
4.	P <sub>4</sub>	1:5	25	45	0.80
5.	P <sub>4</sub>	1:5	28	29	0.60

PROPERTIES OF PAN-CO-MA OF DIFFERENT MOLECULAR WEIGHTS

Polymer	Intrinsic viscosity ( $\eta$ ) dl/g	Elution volume ml	Maximum solubility	Precursor		Carbon fibre	
				T.B. $\times$ M $\times 10^{-3}$ psi	T.B. $\times$ M $\times 10^{-3}$ psi	T.B. $\times$ M $\times 10^{-3}$ psi	T.B. $\times$ M $\times 10^{-3}$ psi
P <sub>1</sub>	2.550	51	12.14	68.66	1.08	101	20.8
P <sub>2</sub>	1.965	50, 58.5, 59	19.0	51.68	0.504	90	14.92
P <sub>3</sub>	1.110	51, 55, 59	22.0	49.60	0.720	85	19.00
P <sub>4</sub>	0.95	52, 56, 60.5	27.0	30.88	0.486	100	10.00

\* P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub> are prepared at 35, 45, 50 and 60° respectively.

### 3.4 Effect of additives, solvents etc. on fibre properties

Maximum concentration<sup>26</sup> of the polymer in the dope is preferred to minimise the voids in the fibres, which are generally drawn from solution of

low dope concentrations. To facilitate the spinning processes conditions like deaeration, extension, increase in solid content, dope viscosity modifiers like aryl or alkyl secondary amino hydrochlorides have been made use of<sup>10</sup>. The coagulation bath consists of DMF and water at varying proportion and the optimum concentration has been fixed at 50% DMF-water.

Wet spinning is a three component system of polymer, solvent and non-solvent in which two transitions, namely gelation and phase separation, occur. Kinetically, gelation is no doubt a slow process compared to phase separation but it is not always possible to design conditions so that the phase separation could be preceded by gelation. However, gelation rate is sensitive to temperature, thermal history and additives. A few studies on the effect of additives to produce gelation during spinning were carried out<sup>11</sup>. For this purpose, a non-solvent and a gelling agent - an inorganic compound - are made use of. The effect of these additives produced interesting results on the cross-section of fibres, not reported earlier. All the spinning conditions being the same, the cross-section of the fibre is 'bean' shaped when an organic additive is added. When an inorganic additive is added, the cross-section is almost 'round'. Same is the case in the case of addition of non-solvent and without any additive<sup>12</sup>. Looking at the mechanical properties<sup>13</sup> of the fibre, the tensile strength and Young's modulus are minimum when an organic additive is added and maximum when an inorganic additive is added. In the case of non-solvent and without additive, the values are almost the same. When a mixture of all the additives is added, the tensile strength and modulus are definitely more than those obtained without any additive and in the presence of non-solvent and an organic additive.

The round shape of the fibre is due to the difference in diffusion of solvent and non-solvent through the solidified skin of the fibre after coagulation and the rate at which such diffusion occurs. A similar situation has been encountered<sup>14</sup> in the case when HCl or acetic acid or oxalic acid is added to the spinning bath whereby the pH of the spinning bath varies from 2.3 to 7. When the pH of the bath solution is less than 3, the fibre attained bean structure whereas at pH 6 it was round. An attempt was made to study the effect of pH of the dope solution and it was found that when an organic additive is added the pH is 4.15 where the bean shaped cross-section of the fibre was observed<sup>15</sup>.

When an inorganic additive is added the cross-sectional shape is round at the pH 11.96 and in the case of non-solvent the pH of DMF (used for making dope solution) is 11.5. These values show clearly that the cross-sectional shape of the fibre is dependent on the pH of the DMF solution used for preparing the polymer dope. When it is acidic it is bean shaped and when it is basic or neutral it is round shaped.

EFFECT OF ADDITIVES ON THE PROPERTIES OF PAN-CO-MA

Additive	Concentration %	Elongation %	T.B. $\times 10^3$ psi	Modulus $\times 10^3$ psi	Shape of the fibre
A <sub>1</sub> (organic)	0.6-6	5.7	23.36	0.6	Bean
A <sub>2</sub> (inorganic)	0.1-2	4.9	48.28	1.2	Round
A <sub>3</sub> (non-solvent)	0.1-1	5.7	34.17	0.7	Round
O (without additive)	...	5.6	30.62	0.75	Round
M (mixture of all additives)	...	5.7	48.98	1.60	Bean

pH VALUES OF DMF AND ADDITIVE SOLUTIONS

Solution	pH
DMF	11.7
DMF + 1% water	11.6
DMF + 56-15% water	7.8
DMF + Organic salt	4.15
DMF + Inorganic salt	11.96

The stretch baths mainly consisted of water. Water acts as plasticizer during stretching of the fibre. With the hydrophobic repulsion of the fibre it might be surprising to see plasticizing action of water. But once free volume has been created by strain or temperature to allow entrance of water into the fibre, it acts as strong plasticizing agent. Plasticization here is meant to denote decrease in the resistance of the fibre to an imposed stress by the liquid water. Plasticization is governed to some extent by the molecular volume and dipole moment of the liquid. Hence, to increase plasticization some amount of DMF is also added to water in the stretch baths. After the fibre passes through the stretch baths, the DMF content in the fibre is considerably reduced but the fibre looks porous. Passing over to the godet heater, the fibre undergoes collapse process, the porous nature of the fibre is eliminated and the porous structure is no longer evident. This is influenced by the moisture content in the fibre, temperature of the godet heater and time of contact of the fibre.

Considerable efforts were put forth to improve the fibre properties by changing the conditions of spinning and a second stage hot stretching above

PROPERTIES OF OLBI ACRYLIC FIBRES

Sl. No.	Diameter	Tensile strength $\times 10^3$ sp.	Elongation %
1.	17.6	97.6	4.0
2.	30.0	100.7	4.0
3.	18.25	100.3	4.0
4.	18.5	104.1	4.0
5.	---	104.2	4.0
6.	17.0	106.7	4.0
7.	---	107.07	4.0
8.	18.76	109.62	4.12
9.	---	112.0	4.0
10. (Porway)	12.11	66.0	3.1
11. (Dolan)	14	76.0	3.0
12. (Bastou)	18	66.0	3.1
13. (Herculen)	18	37.42	3.0

100° using different stretch baths separately. The fibre properties improved and in certain cases excelled even over the imported fibres.

Some of the fibres have been carbonized at 1000° and the properties of such carbon fibres are comparable to those obtained from imported PAN fibres under similar conditions.

PROPERTIES OF CARBON FIBRES FROM OLARI PRECURSORS

Sl. No.	Tensile strength $\times 10^6$ (psi)	Modulus $\times 10^6$ (psi)	Carbon yield
1.	40.77	1.28	—
2.	57.59	5.80	54
3.	62.79	1.66	—
4.	62.56	1.81	—
5.	62.70	10.72	—
6.	70.80	18.64	62
7.	76.80	12.98	—
8.	77.70	10.12	—
9.	80.66	12.15	51
10.	83.01	18.61	50
11.	94.20	19.68	—
12.	98.60	20.00	54.26
13.	100.00	20.20	51
14.	104.5	10.40	50.5
15.	175.4	22.95	—
16.	184.0	19.18	—

Considerable improvement could be achieved by reducing the diameter of the precursor fibres during the second stage of hot drawing as well as spinning under clean room conditions.

#### 4. Applications of carbon fibre reinforced plastics

There remains, no doubt, that carbon fibre reinforced polymers (CFRP) with their extremely high stiffness and low density will replace metals in most future applications where weight saving is the main goal. The only problem is that manufacturing of cars from metal is highly rationalized in industrialized countries, whereas the present production methods of composites still causes high labour costs. Carbon fibre is available in the market in different forms, such as mats, tapes, free fibre in a tow, chop strand mats, felts, springs etc. The recent applications of CFRP are in the aeroplanes and aerospace vehicles. The composite technology offers therefore a great chance for developing countries with high labour capacity.

In human surgery also, carbon fibre reinforced composite will play an important role in future. Bone plates in osteosynthesis<sup>11-12</sup> are one example because of the possibility to tailor the mechanical properties and thus to match the special need controlled by the elastic behaviour of bones. In case of CFRP as material for tools in surgery, one utilises the additional advantage that neither carbon nor polymers absorb X-rays and improved X-ray images can be taken *in situ* during operation. The isotropic form of polymeric carbon, the glossy carbon, is a corrosion resistant impervious material. This material is used in human medicine because of its outstanding bio-compatibility, as electrodes,

percutaneous leads, dental and joint implants. The most striking success of monolithic carbon is achieved with its application as heart valve components. The anisotropic form of polymeric carbon fibres can be applied for replacement of ligaments and tendons. The inferior variety of carbon fibres find their use in the manufacture of sports goods like badminton and tennis racquets, golf clubs and racing bicycles.

#### 5. Future projection

Carbon fibres can be produced in a number of ways from a variety of starting materials and their character is strongly influenced by the manufacturing techniques employed. The demand for carbon fibres is growing apace, both in terms of quantity and area of application. Consumption is currently around 450 tonnes/year increasing at approximately 50 per cent per year. The world market is likely to reach 1000 tonnes/year in 1981-82 and the prospects thenceforth look extremely good<sup>13</sup>. Continued development in aerospace and industrial is likely to push annual production requirements upto several thousand tonnes. Production is located mainly in three countries, viz. Japan, USA and UK with 40 per cent world output from USA.

India today ranks foremost among the developing countries in resin production. Until 1955, phenolic moulding powder was the only raw material made in India. Today, we have several units for the production of various types of plastics such as polyethylene, polyester, nylon etc. At present a large scale utilisation of these plastics are envisaged for the production of composites. It is imperative that the chemists and technologists should jointly venture for new application of reinforced plastics for various applications. It is the chemist's part to develop suitable precursor materials and the technologists part to design suitable processes for the production of carbon fibres for various applications.

#### References

1. R. M. GILL, "Carbon Fibres In Composite Material", Butterworth and Co. 1979.
2. J. LURIN, "Handbook of Fibre Glass and Advanced Plastic Composites", Van Nostrand Reinhold Company, 1969.
3. A. SHINDO, Y. NAKANISHI and I. SONA, *Appl. Polym. Symp.*, 1969, 9, 271.
4. J. E. BAILLY and A. J. OLARKER, *Chem. Ind. Brit.*, 1970, 6, 484.
5. J. H. BARR, B. CHAWASTIAK, R. DIDCHENKO, I. O. LEWIS, R. T. LEWIS and J. B. SINGER, *Appl. Polym. Symp.*, 1976, 29, 161.
6. L. S. SINGER, U. S. Pat., 4,005, 183, 1977.
7. BAYER A. G., B. P., 1,859, 764 (West Germany) 16th April 1971.
8. S. MIWAKA, *Chem. Econ. Engng. Rev.*, 1970, 8, 43.
9. E. FITZER, J. KALKA, *High Temperatures High pressures*, 1971, 3, 68.
10. E. FITZER, K. H. GRIGL, W. HILTMAN, *Proc. 6th London Int. Carbon and Graphite Conf.*, 1970, Vol. 1, p. 493.
11. G. M. JENKINS and K. KAWAMURA, (to Ocul Industry), U. K. Pat., 1228910, 1971.

12. H. M. ELZKIMI and R. B. SPAIN, U. S. Pat., 6, 898, 774, 1970.
13. O. P. BAHL and L. M. MANOCHA, *Fibre Science and Technology*, 1976, 9, 77.
14. T. KOYAMA, M. ENDO and Y. ONUMA, *Jap. J. Appl. Phys.*, 1972, 11, 446.
15. W. G. PARKS and M. PRTRARKA, *Text. Res. J.*, 1966, 25, 780.
16. W. HOFFMAN, M. WITANOWSKI, *Chem. Ind.*, No. 46, 1960, 96.
17. A. SHINDO, Y. NAKANISHI and I. SONG, "High Temperatures Resistant Fibres from Organic Polymers" (Ed.) J. PRINSON, Interscience, New York, 1969, p. 271.
18. Union Carbide Corp., U. S. Pat., 3488, 161 (6-1-70).
19. M. M. TANG and R. BACON, *Carbon*, 1964, 2, 211.
20. K. MYAMICHI, U. S. Pat., 86, 89140, 1972.
21. M. L. LIEBERMANN and G. T. NOLKS, *J. Mater. Sci.*, 1972, 4, 664.
22. A. H. KRUGLER and J. E. MASSIE, U. S. Pat., 12, 26, 878, 1971.
23. C. R. SCHMITT and O. R. TRNU, U. S. Pat., 8, 601, 672, 1971.
24. W. WATT, *Proc. Roy. Soc. London*, 1970, 5A, 319.
25. D. W. MCKER and V. J. MIMHAULT, "Physics and Chemistry of Carbon", Marcel Dekker Inc., New York, 1973, Vol. 8, p. 162.
26. A. SHINDO, R. FUJII and M. SENGOKU, *Jap. Pat.* 4406, 1962.
27. W. WATT, L. N. PHILLIPS and W. JOHNSON, *Engineer*, London, 1966, 221, 816.
28. *Brit. Pat.*, 112804, 1968.
29. M. GRASSIE and J. HAY, *J. Polym. Sci.*, 1962, 56, 189.
30. J. W. JOHNSON and D. J. THORNE, *Carbon*, 1969, 7, 669.
31. M. GRASSIE, "The Dehydration of Copolymers", Monograph No. 20, 191, London 801, 1967.
32. E. FITZER and D. J. MÜLLER, *Carbon*, 1976, 13, 69.
33. (a) E. FITZER and M. HRYM, *Chem. and Ind.*, 1976, 16, 633.
34. W. WATT and W. JOHNSON, *Nature*, 1976, 257, 210.
35. G. G. RADHAKRISHNAN, T. NAGABHUSHANAM, K. T. JOSEPH and M. SANTAPPA, *Makromol. Chem.*, 1979, 180, 2923.
36. R. MORRISON and W. WATT, *Carbon*, 1974, 12, 543.
37. D. E. CAGLIOSTRO, *Text. Res. J.*, 1960, 50, 632.
38. O. P. BAHL and L. M. MANOCHA, *Carbon*, 1974, 12, 417.
39. O. P. BAHL and L. M. MANOCHA, *Carbon*, 1976, 13, 297.
40. O. P. BAHL and L. M. MANOCHA, Paper presented at FRP Symposium, Madras, 1976.
41. O. P. BAHL and L. M. MANOCHA, *Fibre Science and Tech.*, 1976, 9, 77.
42. O. P. BAHL and L. M. MANOCHA, *Die Ang. Mak. Chem.*, 1978, 67, 11.
43. O. P. BAHL and L. M. MANOCHA, *Die Ang. Mak. Chemie.*, 1979, 75, 197.
44. O. P. BAHL and L. M. MANOCHA, B. S. CHAKI, G. O. JAIN and G. BHALLA, *J. Sci. and Ind. Res.*, 1979, 12, 81.
45. L. M. MANOCHA and O. P. BAHL, *J. Fib. Sci. and Tech.*, 1980, 13, 199.
46. B. O. BENNETT and D. J. JOHNSON, *Proc. 5th London Int. Carbon and Graphite Conference*, Vol. 1, p. 377.
47. B. OTTANI, A. YOKOYAMA, A. NUKUMI, "High Temp. Resistant Polymers", Interscience, New York, 1969, 811.
48. T. ARAKI and B. OGI, "Applied Polym. Symp.", 1969, No. 9, 831.
49. B. OTTANI, *Carbon*, 1966, 3, 31.
50. R. B. FORSYTH, *Proc. 10th National BAMPE Symposium*, April 1974.
51. A. ARITA, K. OSAPUNE, Y. YAMADA, H. KAKIYAMA, H. HONDA, N. TAGAWA and S. ABE, *Rep. National Ind. Res. Inst.*, Kyushu, No. 19, 1977.
52. J. L. WHITE, *Aerospace Report*, No. T. R. 0074 (4260 40), 1, 1974.
53. R. BACON, *Phil. Trans. R. Soc. London*, 1950, A294, 583.
54. J. E. MCINTYRE (personal communication).
55. G. G. RADHAKRISHNAN, K. T. JOSEPH and M. SANTAPPA, Paper presented at National Seminar on New Industrial Polymers, AC College, Madras, 1981.
56. (a) G. G. RADHAKRISHNAN, K. T. JOSEPH and M. SANTAPPA, *Leather Sci.*, (in press).
57. J. P. KNUDSEN, *Text. Res. J.*, 1961, 34, 933.
58. N. JOSEPH, A. K. MURTHY, K. T. JOSEPH and H. RAMANATHAN, Paper presented at International Symposium on 'New Frontiers in Polymeric Solids and Polymer Applications', Madras, 1980.
59. N. JOSEPH, A. K. MURTHY, K. T. JOSEPH and M. SANTAPPA, *J. Macromol. Sci. Chem.*, (in press).
60. N. JOSEPH, A. K. MURTHY, K. T. JOSEPH and M. SANTAPPA, *Leather Sci.*, 1981, 28, 177.
61. V. GROH and R. GIESKE, *Faserforsch. Textiltech.*, 1969, 20, 30.
62. Research Project OL VG 118A, ZK/NT/MT 200, supported by German Government BMFT.
63. H. BRÜCKMANN, Thesis, University of Karlsruhe, West Germany, 1979.
64. E. FITZER, W. HÜTTNER, L. KINZLEY and E. GILES, reprint, 14th Biennial Conf. on Carbon, Penn. State University, 1979, p. 58.
65. E. M. TRUWIN, *Shell Polymers*, 1979, 3, 47.