INDIAN CARBON FIBRE HISTORY AND PRESENT CHALLENGES

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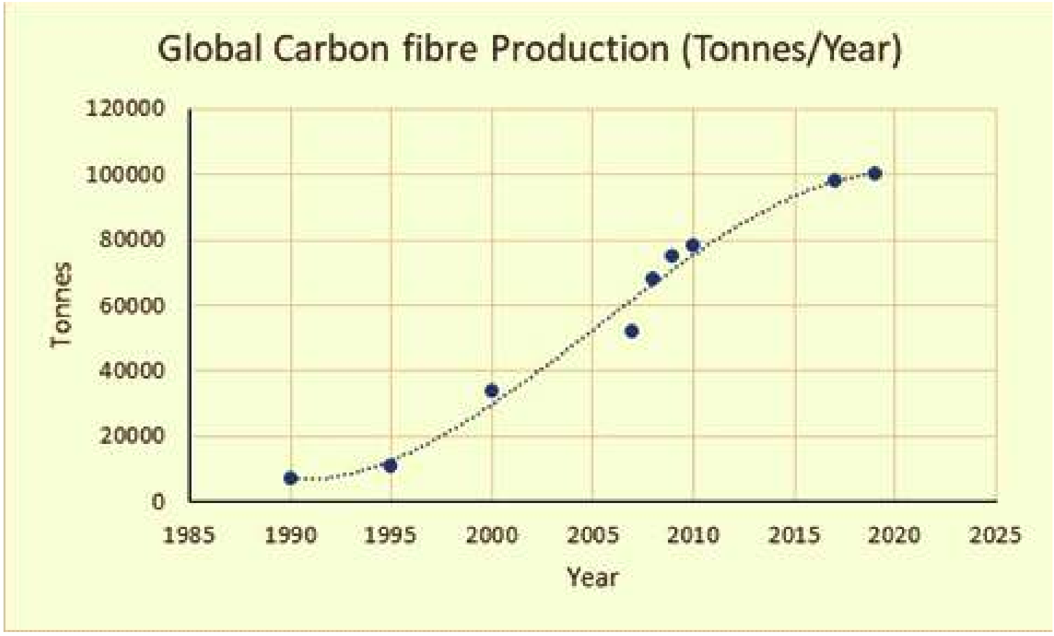
Introduction

Carbon fiber is a unique material among high-performance fibers which is used for aerospace to industrial applications. It consists of majorly carbon (>95%) with some amounts of other elements such as oxygen, nitrogen, etc. The importance of carbon fiber is derived from its high tensile properties such as strength, modulus, and low elongation to stress. If specific strength is compared, this amazing material is fifty times stronger than steel. The specific strength of steel is ~60 kN.m/kg and that of carbon fiber is about 3000 kN.m/kg. When carbon fiber is used in aircraft, 20% of its weight can be reduced compared to aircraft with aluminum which is very important for better fuel efficiency and higher payload. 40% of the structural weight of aircrafts are made of carbon fiber composites. Apart from high-end aerospace applications, carbon fiber finds its place in industrial and sports goods. It is used in bridge repair, sports cars, tennis rackets, lightweight bicycles, etc.

Dramatic growth in worldwide production and consumption of carbon fibre is being witnessed due to the large demand for carbon fibre in the fields of sports and leisure sector, automobile industries, civil and marine engineering apart from its conventional application in the aerospace industry. The following figure gives an idea of the growth in carbon fibre production worldwide in the last thirty years [1,2]. There has been significant growth in industrial carbon fibre production especially large tows carbon fibres such as 24k and 48k.



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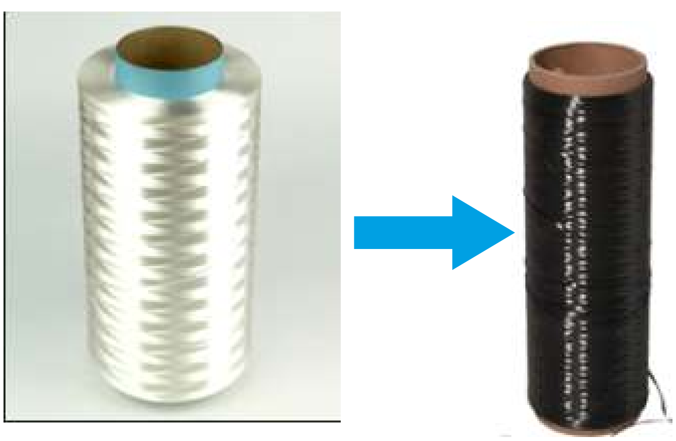
History of Carbon Fibre

Worldwide

In 1860, Joseph Swan and in 1879 Thomas Edison produced carbon fibre and found application as the filament in a light bulb. Cellulosic fibres were charred to produce carbon fibre those days. Edison used cotton fibres and heated at very high temperatures in an inert atmosphere to remove all elements except carbon. In 1958, Roger Bacon from Union Carbide produced the high-performance carbon fibres using viscose rayon. These continuous carbon fibres were made by heat-treating rayon at high temperatures in an inert atmosphere until all other elements except carbon were eliminated. In the early 1960s Japanese scientist Akio Shindo developed Polyacrylonitrile (PAN) based carbon fibres which lead to today's high tenacity acrylic precursors and high strength carbon fires such as T-300 and other carbon fibre variants. During the 1960s United Kingdom-based Courtelle, Japanese Toray, and American company Union Carbide were the major players in carbon fibre production. After year 1970, several manufacturers started production of carbon fibre across the world including Mitsubishi (PAN and pitch-based), Toho Tenex, Zoltek, Cytec, Aksa, etc. Recently China also is a major producer of carbon fibre. Today 95% of the world carbon fibre is being manufactured from acrylic precursors. The remaining 5% is being produced from viscose rayon, pitch, etc.



Acrylic Precursor Carbon Fibre

India's encounter with Carbon fibre

In India, Indian Petrochemical Corporation Ltd (IPCL) was producing carbon fibre since 1989 under the trade name Indocraft. It had a production capacity of 12 metric tonnes. The plant was closed down in 1998 due to non-availability of precursor fibres. Also, 12 MT is not economically viable. IPCL was importing the PAN precursor from Courtelle, Mitsubishi and others. Today, an economically viable production capacity is 1500 Tonnes per annum.

Though, India had nearly ten years of experience in small scale carbon fibre production at IPCL, India is yet to commercially produce good quality acrylic precursors suitable for T-300 and above carbon fibres. Carbon fibre and precursor technology are not available as the material is extensively being used in defence applications. Carbon fiber producers do not disclose how their product is manufactured. The United States require carbon fibre manufacturers to secure an export license for each carbon fibre transaction with foreign interest. Most of the machinery and precursor technology falls under the export control rules where such critical technologies are regulated and restricted.

Carbon fibre research in India

Academic research

India's carbon fibre research started as early as 1980 at National Physical Laboratory, (NPL), Delhi. These researches were primarily led by three scientists, O. P. Bahl, L. M. Manocha and R. B. Mathur [3,4] Their work majorly focused on the characterization of commercially available precursors, their chemical modification, the effect of stabilization processes and carbon fibre properties. In the same period of time, researchers at Indian Institute of Technology, Delhi (IIT) published work on the synthesis of Polyacrylonitrile, their copolymers and fibres [5]. Some basic research on acrylic precursors also happened in Central Leather Research Institute (CLRI), Madras [6]. After the carbon fibre plant at IPCL was commissioned, there was an urgent need of acrylic precursor. The plant was offered precursor for a limited time (five years) due to restrictions. India was supposed to create the precursor facility by that time. The Government of India identified several institutes for precursor research and development. IPCL had an acrylic fibre plant those days which was producing textile grade acrylic fibre. Textile grade acrylic fibres are low strength having comonomers suitable for dye sites. Precursor grade acrylic fibre has to be high tenacity and devoid of bulky groups used for attracting cationic dyes. Precursors should have monomers with carboxylic acid groups to facilitate thermo-oxidative stabilization (Initiation of nitrile cyclization) in an air atmosphere [7]. Given the above IPCL R&D also initiated precursor research [8].

In the meantime, in 1993, a major turning point in precursor research happened when a joint project funding was sanctioned to IIT Delhi by Department of science and technology (DST) and Aeronautic Research and development board (ARDB), Government of India. The project amount was about one crore rupees. The project was headed by Prof. Pushpa Bajaj, Prof. A K Gupta and Prof. Kushal Sen [9] at the Department of Textile Technology, IIT Delhi under the close monitoring of Dr A P J Abdul Kalam, then scientific advisor to defence minister.

Mission mode development at IIT Delhi (1993-1998)

The major focus of the DST/ARDB sponsored project was the development of high tenacity acrylic fibres as a precursor for carbon fibre. Table 1 shows the properties of commercial precursors. Precursor with similar properties may provide carbon fibres with quality equivalent to T300.

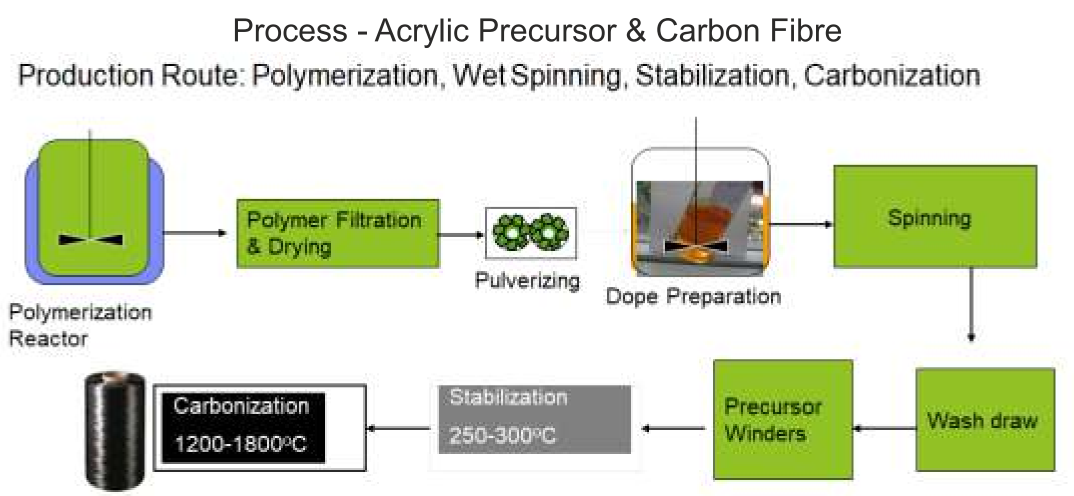
Table 1- Properties of PAN Precursor Fibres.

Property	Commercial Precursor I	Commercial Precursor II
Probable Polymer composition	AN/MA (98:2)	AN/MA/MAA (96:3:1)
Intrinsic Viscosity (dl/g in DMF) at 25°C	1.64	1.6
Filament diameter (µm)	12	11.4
Denier/ Filament	1.21	1.1
Density (g/cm^3)	1.184	1.182
Tensile strength (GPa)	0.68	0.66
Initial Modulus (GPa)	12.2	8.25
Breaking elongation (%)	11	16
Extent of order (%)	59	47
Molecular orientation (%)	86	83
Exothermic initiation Temp (°C)	205	200
Exothermic Heat (ΔH) (J/g)	2602	2315

The precursor produced by any carbon fibre manufacturer differs from those of its competitors, and the processing details that give each brand its signature characteristics and are considered to be their intellectual property. Carbon fiber manufacturing process is difficult to copy and any professional consultation is very expensive. The availability of experienced manpower in this filed also is very rare. Only very few manufacturers offer precursor production line and there are only a few organizations which provide oxidation oven and carbonization furnace. The whole manufacturing facility or manufacturing line is capital intensive. It can be in the tune of 700 crores for a 1500 tonnes per annum plant. It can take up to two years for complete installation and commissioning of the line to make it operational. The team at IIT Delhi headed by Professor Bajaj published several research papers on the production of precursor and carbon fibre [8,10,11,12]. It is evident from their publications that they made significant achievements in the synthesis of high molecular weight co- and terpolymers of polyacrylonitrile (PAN). The comonomers used are vinyl acids and esters mentioned in Table 1. The vinyl comonomers facilitate the easy drawing of filaments during spinning and thermo-oxidative stabilization during PAN to carbon fibre processes. Several methods of polymerizations were attempted including solution polymerization [13], emulsion polymeriztion [9] and solvent water suspension polymerization [14]. In these papers, they have reported the synthesis of PAN with Methyl acrylate (MA), Methacrylic acid (MAA) and Itaconic acid (IA) comonomers. Intrinsic viscosities in the range of 1.2 to 3dl/g were reported depending on the polymerization method with molecular weight distribution (Mw/Mn) as low as 2.5. A fibre spinning (wet and dry-jet-wet) machine was installed at IIT Delhi with coagulation, washing, drawing and winding systems. High tenacity acrylic precursors of strength as high as 0.65 GPa were reported by IIT Delhi team in the year 1998 [11]. The institute also reported some efforts on stabilization and carbonization of PAN precursor to produce carbon fibre.

The project was discontinued from IIT Delhi in the year 1998 and further research was initiated at National Aerospace Laboratory, Bangalore.

After concluding the project at IIT Delhi, a new project was initiated at NAL. With the focus on indigenizing the carbon fiber development from polyacrylonitrile based precursor fiber, CSIR-NAL established an integrated facility for carbon fiber and prepregs in 2003 with the leadership of Shri M K Sridhar. NAL claims to have developed a process for making carbon fibre equivalent to T-300 or above and certified by CEMILAC for standard modulus grade carbon fiber production. CSIR-NAL is



Development of Carbon Fibre at National Aerospace Laboratories (NAL), Bangalore

now offering this standard modulus grade carbon fiber technology, certified by Centre for Military Airworthiness and Certification, to any Indian organization. The followings are the complete process and properties of carbon fibre as per the NAL website [15].

a. *Acrylonitrile polymerization (CSTR mode)*
b. *Carbon fiber precursor by wet spinning*
c. *Heat treatment of precursor fibers to carbon fibers*

Standard modulus grade carbon fiber properties:

Filament Count	Tensile Strength [GPa]	Tensile Modulus [GPa]	Filament diameter [µm]	Density [g/cc]	Carbon [%]
6K	3.5±0.1	240	7.0	1.78	>94

The technology was transferred to Kemrock Industries and Exports Ltd, Vadodara. Kemrock created a 300 TPA facility in 2011 at their composite manufacturing centre which included systems for suspension polymerization, thermo-oxidative stabilization and carbon fibre processing. Kemrock, however, could not commercially produce and sell carbon fibre of required properties in the domestic or international market. Kemrock, later on, stopped all their operations including composite manufacturing. In the year 2017-18, Kemrock was taken over by Reliance Industries Ltd and renamed as Reliance Composite Solutions. Reliance started manufacturing glass fibre composites in 2018 and reports are that they are working on operationalizing the carbon fibre production facility.

NAL continued to progress in improving the properties of their carbon fibre and in a recent expression of interest in January 2019, NAL intent to operate their 3TPA plant in a continues process through GOCO model.

Carbon Fibre Research at Indian Space Research Organization

Carbon fibre is one of the essential materials in space technology. Large-scale rocket parts of more than eight meters in diameter are made of carbon fiber skins with an aluminium honeycomb core. For reentry, *Orion* multipurpose crew vehicle uses a 5-meter diameter carbon fiber heat shield that is manufactured as a sandwich structure featuring carbon fiber skins and a titanium honeycomb core. Similar ablative material was used for the *Apollo* missions also [16]. Indian space research organization (ISRO) also uses carbon fibre in several rockets and satellite parts. To fulfil the internal requirement of ISRO, a team of scientists lead by Dr C P R Nair worked on the development of acrylic precursor. Several reports were published in international journals in this regard [17]. The main focus was on the synthesis of various copolymers, dope rheology, the effect of temperature etc.

Economics

The quality of carbon fibre produced depends on the quality of precursor fibre. Quality of precursor depends on the quality of the polymer. So, it is important to have the right kind of polymer and precursor to produce good quality cost-competitive carbon fibre. The quality of polymer and precursor properties influence the process temperature and speed of production. Both these parameters will decide the final price of carbon fibre. The scale of production is also an important deciding factor on the selling price of carbon fibre. 1500 TPA is the typical scale for commercial production of carbon fibre. Carbon fibre production is a very energy-intensive process and an increase in nitrile cyclization temperature, pre-carbonization and carbonization can affect the carbon conversion, process speed and resulting carbon fibre properties. Thus, before establishing a carbon fibre business, it is important to understand the commercial scalability of the technology. The cost of production of carbon fibre is important when a material has to compete with imported and time-tested products from Toray, Mitsubishi, Zoltec etc. It is important to understand what is the conversion of carbon fibre or how much carbon fibre can be produced from 1 kg of PAN precursor. The conversion is primarily related to the composition, molecular weight, molecular weight distribution, fibre denier, strength, processing temperature and treatment time, etc (Table 1).

If a production capacity of 1500 TPA carbon fibre of quality equivalent to T-300 and a net profit of 10% and 20% are considered, following calculation shows that the simple payback period is about 14 years.

Commercial Production Capacity	*-*	*1500 TPA*
Cost of T-300	-	$ 22/ kg
Net Profit margin @ 10%	-	$ 2.2/kg
Total Profit/ year	- -	1500 x 1000 x 2.2 $33,00,000
In Rs-	~	25 crores
If net profit margin @ 20%	-	$4.4/ kg
Total Profit/ year	- -	1500 x 1000 x 4.4 $66,00,000
In Rs-	~	50 crore
Capital Investment	-	700 crores
Simple Pay Back	-	14 years

Simple payback of fourteen years is huge. The industry usually considers three to five years a viable payback period. To make it more attractive to business, the profit margin has to be increased by reducing production cost.

Carbon fibre production is an energy-intensive process. 40-50% of the cost of carbon fibre is due to the precursor. The precursor cost is about $3-4/kg. Minimum of wo kilograms of the precursor is required for preparing one kilogram of carbon fibre. The remaining cost is for thermal stabilization, carbonization, surface treatment etc. Thermo-oxidative stabilization is done at 200-250°C, pre-carbonization at 600-800°C (LT furnace) and carbonization at 1200-1800°C (HT furnace). A massive portion of the cost of production is associated with the energy required for the process mentioned above. According to an analysis, only China electricity rate/ unit supports sustainable carbon fibre production. Approximate cost of electricity in China, United States and India are Rs-3, 6 and 8/kWh. To link with the global benchmark, subsidized electricity is required. It is also important to have uninterrupted power supply during the heat treatment process. Any power failure will reduce the processing temperature, stabilization and carbonization process will not be completed leading to reduced mechanical properties.

The main raw material for making acrylic precursor is Acrylonitrile (ACN). It is important to ensure a constant supply of raw materials with consistent quality to produce superior precursor fibres. Reliance Industries Ltd (RIL) was the only company producing ACN in India. The production was stopped for the last several years. It should be revived for a steady supply of quality raw material. Similarly, Dimethyl Formamide is one of the main solvents for PAN. Only limited companies are producing them in India.

Need of Government Support and Conclusion

Indian industry is new to high-performance fibre production. Great effort and support from the government are required to gain industry confidence to initiate production of such materials in the country. The main reasons for the reluctance of the industry to initiate the production of high-performance fibers are:

1. Non-availability of reliable inhouse technology, international technology provider due to export control restrictions and product guarantee.
2. High energy cost makes the business less viable. The government may consider special incentives and special energy pricing for carbon fibre industry.
3. The government should ensure uninterrupted, high-quality power supply.
4. Buyback of carbon fibre produced- The government should come forward to buy all the carbon fibre produced as the domestic requirement is only 300TPA.
5. Support CF composite industry for full capacity utilization- The minimum economically viable production is 1500 TPA and the domestic demand being 300 TPA, it is a must to enhance our carbon fibre composite industry. Special incentives should be considered for both CF and composite industry for some period of time till the business becomes competitive and self-sustainable.
6. Permission for exporting carbon fibre after satisfying internal demand. If any industry produces more than 300 TPA (present demand), they should be permitted to export excess production.

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