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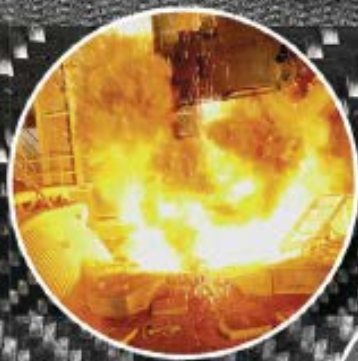
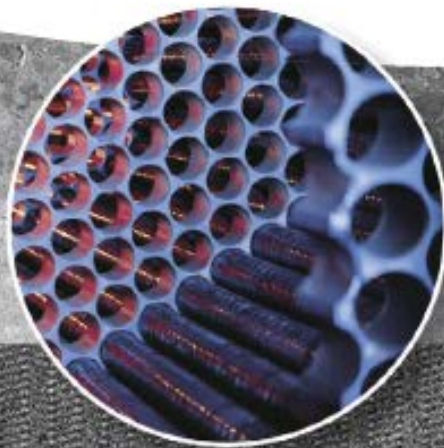
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# Industrial Carbon and Graphite Materials

Raw Materials, Production and Applications



## Fibers, 15. Carbon Fibers

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## Introduction

Carbon fibers are one of the strongest known materials today. In the early 1960s they were highlighted as a "Rider of a New Industrial Revolution" and as an initiator of a new "Carbon

Age". In Europe, the SIGRI Elektrographit GmbH, Meitingen/Germany started in the late 60s one of the first industrial pilot plants in the world.

## ***History***

From historical viewpoint, the development of carbon fibers with sufficient mechanical properties started after noticing an unwanted color change / yellowing of polyacrylonitrile (PAN) textiles at elevated temperatures.

Polyacrylonitrile was one of the polymers like polystyrol (PS), polyoxymethylen (POM), polymethylenmetacrylate (PMMA), Nylon/polyamide (PA6, PA66), polyethylene (LDPE), polyurethane (PU) and others which were developed in the polymer hype period from 1925-1950.

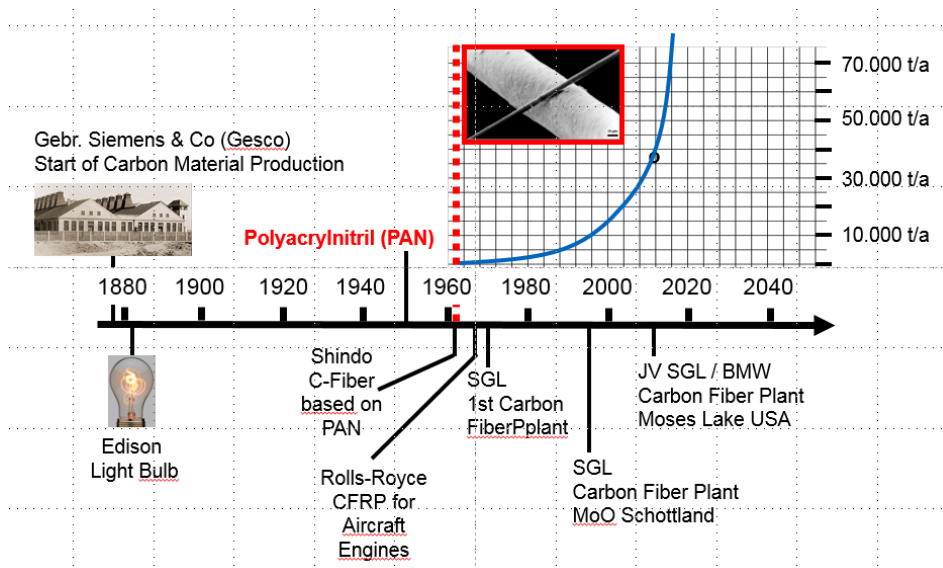
STAUDINGER in 1922 [0-1] initiated this development of polymers with the postulates that there might exist an endless variety of macromolecules based on hydrocarbons. DuPont developed polyacrylonitrile in 1950 [0-2] for textile applications. With the intention to reduce the unwanted yellowing effect of polyacrylonitrile, researchers placed copolymers in the polymer chain, resulting in a contrary effect of increasing the yellowing effect that finally leads to the conversion reactions into carbon fibers.

In this context, we have to mention the work of SHINDO [26, 26-1] who primarily realized the conversion of polyacrylonitrile fibers into carbon fibers. In his patent from 1959, he claimed that the properties of the carbon fibers are dependent on the polyacrylonitrile structure. These first research results from Shindo in the context with other researchers in the 60s W.WATT tried to summarize 1985 by W. WATT in the Handbook of Carbon Composites / Strong Fibers [0-3].

In principle, carbon fibers are available from any carbon containing material. The only basic requirement is a high carbon yield and the formation of graphitic carbon layers with a low defect level in the structure. Historically the first carbon filaments have been available by Thomas EDISON [4] who converted cellulosic fibers based on cotton or bamboo into carbon filament used as incandescent lamp filaments.

Since the late 60s the commercial production of carbon fibers becomes more and more visible starting in Germany with the first carbon fiber production (Figure 0). The technical and commercial breakthrough for high performance carbon fibers started when optimizing the PAN process. This process turned out to be the most important one due to a high carbon yields in combination with an economical process (Figure 0-1) compared with carbon fibers based on precursor materials like mesophase pitch, lignin and cellulose.

PAN based carbon fibers have superior mechanical and physical properties compared i.e. to rayon based ones. Today they are the most important and promising precursor for manufacture of high strength carbon fibers. Carbon fibers based on mesophase pitch turned out as more expansive following a complicated and complex process of conversion of cheap pitches into mesophase forming modifications.

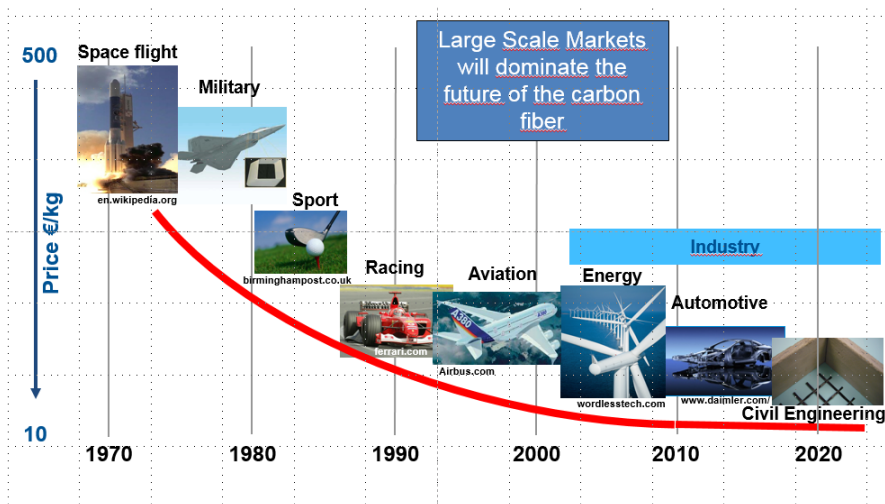


**Figure 0** The history of commercial carbon fibers

	<b>Carbon Yield</b> (ca.)	<b>Material Characteristics</b>	<b>Market Share</b>
<b>Polyacrylonitrile</b>	50 %	Middle / High Modulus High / Very High Strength	95 %
<b>Mesophase Pitch</b>	80 %	Very High Modulus Low / Middle Strength	< 5 %
<b>Cellulose</b>	25 %	Poor because internal Defect Structure	Minimal
<b>Lignin</b>	20 %	Poor because internal Defect Structure	Minimal

**Figure 0-1** Market share of carbon fibers depending on precursor type

Following the rules of market penetration, the increasing volume in large-scale markets influences global availability of commercial carbon fibers with decreasing prices. Actually, it becomes visible that the carbon fiber price comes down to a level which will not be undercut in the near future.



**Figure 0-2** The market penetration and price development of carbon fibers

## ***Fundamentals***

Independent of the precursor type carbon fibers are black in color and have diameters typically smaller than 10  $\mu\text{m}$ . The outstanding mechanical properties results in an ordered structure of carbon hexagons where the carbon atom is  $\text{sp}^2$ -hybridized as consequence of pyrolytic processes.

The strong carbon-carbon atomic bond allows the realization of a high tensile strength in combination with a high flexural modulus. The formation of graphitic layers of carbon are the key for highest mechanical properties (Figure 0-3).

The industrial process steps have to consider this fact and they must ensure a good orientation of the carbon-carbon bonds in the longitudinal direction of the resulting carbon fiber.

From theoretical viewpoint, the mechanical properties of carbon structures (see also chapter 4.1) are calculated with a strength of 100.000 MPa and a Young's Modulus of 1060 GPa (Figure 0-4). Remarkable is the situation that the carbon fiber type with the highest tensile strength (Torayca, T 1000) are known since 1986 with a record value of 7500 MPa that is up to now not overcome.

That means that carbon fibers reach less than 1/10 of the theoretical value since more than 30 years.

It is obvious that since that time any further outstanding developments in mechanical performance seems to stagnate.

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