Carbon Fibres: a Review of Technology and Current Market Trends

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AUTHORS

Roger Wise

TWI Associate Director Dr Roger Wise is a physicist and materials scientist who has spent a considerable part of his career developing joining and other processing technologies for carbon fibre reinforced thermoplastic composites. In this role, he is currently supporting the introduction of these materials into the automotive sector in the UK

Pauline Girard

In 2012 Pauline Girard received a French Engineering degree from the European School of Chemistry, Polymers and Materials Science (ECPM) and a masters degree in the physics of materials from the University of Strasbourg (both based in France). She then joined The Welding Institute (TWI) as project leader within the Advanced Materials and Processes Technology Group. In 2013 Girard began a PhD at the University of Nantes (France). Her research currently focuses on chemistry, photo physics, physical chemistry and nanomaterials.

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Contact

Robert Quarshie

E: robert.quarshie@ktn–uk.org

T: 07964 563 744

The Knowledge Transfer Network,
Business Design Centre, London,
N1 0QH

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1. INTRODUCTION

1.1. SCOPE

This review, initiated by the Knowledge Transfer Network as part of its support for the advanced materials community, was undertaken jointly with TWI. The review is intended to provide those with a current interest in carbon fibres with an entry point to this valuable and highly dynamic materials technology. Literature available on carbon fibres is very extensive and rich, for example the book by Morgan (1), which provides a full account of the technology and some applications, and so this review seeks only to provide some pointers and trends that may help those wishing to understand this field in greater depth. Full references are given at the end of this document if further information is required. Most carbon fibre goes into the manufacture of composites together with a thermosetting or thermoplastic polymer matrix, and a review of this industry in the UK was produced in 2009 (2).

There are several important factors currently affecting the carbon fibre industry and much of the following is intended to allow the reader to begin to understand these changes.

The main factors are:

- The continued expansion in the market, especially in some newer volume sectors such as automotive.

- The drive towards a more cost-effective, high-quality fibre that is manufacturable in large volumes.

- Sustainable carbon fibre sources, including renewable precursors and routes for recycling carbon fibres from composites.

Other associated fields such as the development and applications for carbon nanotubes and carbon whiskers are not within the scope of this document.

In this review, the markets and economic considerations are briefly addressed, followed by a review of physical properties and manufacturing technologies for carbon fibres. These are then used to inform some of the recent trends in technology development and innovation in the final section.

Definition

Carbon fibres are composed of at least 92% carbon and most commonly have a diameter in the range 5–10μm. They are polymers with a structure that is almost completely graphitic — a pure form of carbon in which the atoms are arranged in big sheets of hexagonal rings; this structure provides very high levels of stiffness and strength. Carbon fibres have been produced and improved for many decades because of their excellent mechanical, thermal and electrical properties, often exploited as carbon fibre composites for highly valuable applications in sectors including aerospace, defence, wind energy and sport. Specific examples of applications include aircraft wings, wind turbine blades and tennis rackets.

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2. MARKETS

2.1 GLOBAL TRENDS

Global carbon fibre production was approximately 80,000 tonnes in 2015 (3) and primarily shared between a relatively small number of companies such as Toray, Toho Tenax, Mitsubishi, Cytec, Hexcel, SGL Group, Dow/Aksa, Formosa Plastic and Hyosung. Asia represented 35% of global demand for carbon fibres in 2015, with Europe 34%, North America 25% and the rest of the world, 6%. Although the volume production is dominated by the USA, more of the companies working in the carbon fibres field are based in Japan. In 2005 Toray was the leader in this domain, having 34% of the global market. Carbon fibre production was approximately 20,000 tonnes in 2004 and reached around 70,000 tonnes in 2010 (4), and this impressive increase resulted from a very high interest in these new materials due to their high-performance properties. The main manufacturing companies over this time period remained largely the same and were Toray, Toho Tenax, Mitsubishi, Hexcel, Cytec and the SGL Group (5).

The carbon fibres market in 2012 was estimated to be $10bn. Analysts predict a market of $40bn by 2022 (6). Carbon fibre manufacture is a very profitable business and the major players have invested heavily to produce and improve these materials. For instance, Dow Europe (USA) and Aksa Akrilik Kimya Sanayii (Turkey) created a partnership and invested around $1bn to build a new factory in 2015 that could produce 3500 tons per year, i.e. approximately 8% of the global market at that time. Another agreement has been signed between SGL Carbon and BMW representing $307m. These sums highlight the value and the importance of this business (6).

In the 1970s, the main application of carbon fibres was sports equipment but since 1985 aerospace and other industrial applications have been developed. Nowadays, many industry sectors use these materials, and further market expansion is predicted in the construction, automotive, wind energy and offshore fields (4). In 2007, Toray had 59% of its production consumed by industrial applications, 20% by aerospace and 21% by sports equipment applications. By 2011, this had changed for Toray to 41% of the production for aerospace, 38% for diverse industrial applications and 21% for sports equipment (7). A market analysis was conducted in 2012 (3) to estimate the future growth of several markets linked to carbon fibres. According to this review, the demand in aerospace will increase by 40% during the next 9 years. For industrial components, the review predicted 240% growth, with energy applications dominating this space. Consumer products will grow a mere 25% in the next 10 years. By 2020, the prediction is that industrial uses will dwarf all others, with automotive the largest.

The price of carbon fibres varies according to performance and volume, with the costs for the industrial and automotive market considerably less than those for aerospace. For example, the price for ultra-high modulus fibre has been quoted as high as $900/lb (£1,200/kg) with standard modulus fibre as low as $10/lb (£13/kg). Costs as low as $5/lb (£7/kg) are currently being projected, which will result in much wider use in the automotive industry. In the new BMW cars with major carbon fibre components, €100/kg (£80/kg) for actual components is reported, with €20/kg (£16/kg) being the material cost (8). Cost differences resulting from different production locations are also reported (8).

2.2 VALUE CHAIN

From the following analysis of the manufacturing steps in sections 5 and 6, a simplified overview of the value chain for the production of carbon fibre composite components is shown in Figure 1. An alternative approach is presented in another recent report (2).

In general, the large carbon fibre producing companies will be heavily involved with the first four steps in the chain. End users, such as aircraft manufacturers, will be involved in the composite processing and assembly,

Precursors	Process	Finishing (surface prep. or sizing etc.)	Weaving and Prepregging	Composite processing	Finishing (coating, assembly etc.)	Recycling
High value pitch and PAN: Purity is of paramount importance and value because impurities result in defects in the final product. Much research is currently ongoing to develop low cost precursors	With pitch and PAN complex, difficult to manage processes produce high value fibres at high cost	Chemical treatments can be carried out to increase surface area and improve chemical bonding to resin matrix of composite.	Full wetting of the fibres with the resin is generally critical to achieving components with good mechanical integrity	Conversion of prepreg or tape into composite products by resin transfer moulding, tape lay or autoclave for example	Composite components often require surface protection and the means to assemble them into a structure e.g. bonding, welding or mechanical fastening	Increasingly important for end-of-life vehicle in automotive.

Figure 1 Simplified overview for the value chain of a carbon fibre composite component derived from the review in sections 5 and 6.

and the recyclers are typically specialist companies that are developing rapidly to meet product end of life requirements and legislation. There are considerable barriers to entry for organisations wishing to become manufacturers of carbon fibre. These include the high cost of chemical plant involved, high levels of technical expertise required, and the provision of a production site with the appropriate levels of health and safety management and control for the precursor chemicals often involved.

Barriers to entry for those companies wishing to engage in composite processing are lower, but still significant, typically involving investment in equipment such as autoclaves, prepreg handling and heated presses, as well as suitable material testing and analysis capability. A view of opportunities for the UK in this growing market sector are given in section 8 of this review.

2.3 MORE RECENT TRENDS

In 2013, the most notable change in the landscape for carbon fibre market demand was in the automotive sector. Driven by imperatives for weight reduction and greater efficiency, a strong interest in CFRP material and

processing technology has become evident. Although growth is currently relatively modest in this sector, at about 5% of global production for 2013, the projections for 2020 are much more significant (9). To achieve this, the cost of the technology has to be reduced.

Some other early movers such as BMW have already invested in joint ventures with carbon fibre companies, in BMW's case SGL. It is now making its own carbon fibre composite components for its new range of i3 and i8 vehicles.

Along similar lines, Toray has developed a joint venture with Daimler, and in 2014, further strengthened its position with the acquisition of Zoltek, another carbon fibre producer.

In addition, it was reported in early 2014 that electric car maker, Tesla, was talking to GS Caltex about the supply of carbon fibre from South Korea (11).

Automotive Company	Carbon fibre/composite partner	Relationship
Daimler (Mercedez-Benz)	Toray	Joint venture
General Motors	Teijin	Joint development agreement
Zoltec	Magna	Development of CF SMC
Audi	Voith	Development partnership
Ford	Dow-AKSA	Joint development agreement

Table 1 Some commercial relationships developed in the past five years between carbon fibre reinforced composite companies and automotive companies (10)
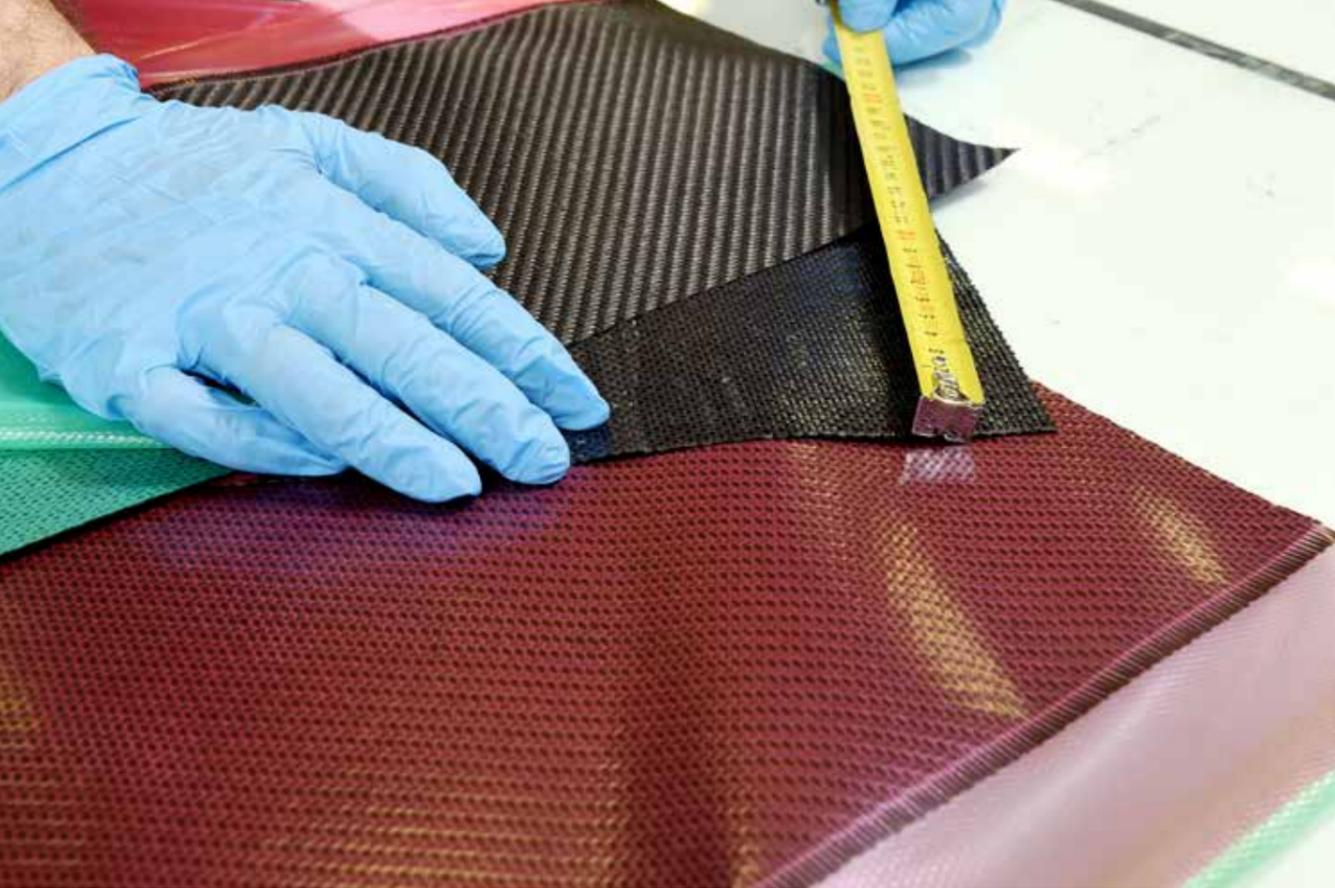
3. PROPERTIES OF CARBON FIBRES

3.1 GENERAL PHYSICAL PROPERTIES

Properties of carbon fibres primarily depend on the precursors, and in general the diameters of the fibres are included in the range of five and seven micrometres with a volumetric mass between 1.74 and 1.95g/cm3. The production is continuous and the fibres are grouped in the form of bundles containing between 1,000 to 48,000 fibres. The carbon fibres are divided into groups according to their elastic modulus and their tensile strength. Five categories are used:

- UHM: Ultra-High Modulus (modulus > 450GPa).

- HM: High Modulus (450GPa > modulus > 350GPa).

- IM: Intermediate Modulus (350GPa > modulus > 200GPa).

- HT: low modulus (modulus < 100GPa) and High Tensile (tensile strength > 3.0GPa).

- SHT: Super-High Tensile (tensile strength > 4.5GPa).

Any material containing carbon can be 'carbonised' by heating it to around 1,000°C but not all carbon materials heat-treated to high temperatures are truly graphitic. Only certain carbons start with an adequately ordered structure to form nearly perfect graphite crystals, and only these graphitic substances can approach the excellent properties of pure graphite such as high thermal and electrical conductivities and high stiffness (12). The properties of the fibres are linked to the carbon yield; the carbon content has to be high to obtain characteristics near to the properties of graphite. Carbon yield depends on several parameters: the nature of the precursor, the rate of heating, the environment and the molecular weight of the precursor (13). For instance, polyacrylonitrile produces carbon fibres with a very small crystal size that offers good flexibility, a very high tensile strength and good electrical conductivity. This is contrary to pitch-based carbon fibres that possess a large crystal size. This characteristic gives stiffness, good tensile strength, excellent electrical conductivity and excellent thermal conductivity. The mechanical resistance varies from 700MPa to 6,000MPa according to the nature of the precursor. The Young's modulus is in the range between 33GPa and 800GPa (14).

Carbon fibres possess several properties of great interest to numerous applications such as high resistance and high elastic modulus in tension, high fatigue resistance, low density (1.6-1.8), high thermal conductivity and stability, corrosion resistance, electrical conductivity and X-ray transparency. All of these features have given rise to great interest from design engineers for many years with the result that these materials are used to produce brakes, blades, cables, medical devices, sports rackets, aircraft structures and many more products.

The one central issue limiting the further widespread use of carbon fibres is the cost, in both money and energy. In fact, to produce 1kg of carbon fibres, 286MJ are required (14). For this reason, many studies are now being performed to reduce the costs of production and the required energy, and with increased interest from the automotive sector, this looks set to continue.

3.2 DEFECTS

Surface flaws include surface imperfections, fibril boundaries, bends and also kinks. They control the strength of carbon fibres that have not been heat treated beyond 1,000-1,200°C (15). These fibres are more brittle than the heat-treated fibres. Bends and kinks tend to straighten out under longitudinal tension and tend to become more severe under longitudinal compression (13).

Internal flaws can be evident in carbon fibres after heat-treatment between 1,000°C and 2,800°C by high-voltage electron microscopy after etching. This experiment allowed the presence of the following internal defects to be detected (16).

- **Central cavities:** These cavities occur along the central axis of the fibres and are elongated along the fibre axis up to about 50μm. The maximum diameter is about 5μm. This defect is probably due to the expansion of gas at high temperature. These cavities involve the reduction of strength by a reduction of the effective cross-sectional area.

- **Diconical voids:** These are present in almost all carbon fibres and are randomly distributed across the cross section of the fibre. Their diameters are in the range between 1 and 3μm. These voids may be caused by small particulate inclusions or by gases dissolved in the fibre-spinning solution or by irregular flow at the spinneret orifice by the rapid coagulation of the polymer.

- **Inclusions:** These defects are generally irregular circular shapes with a maximum size of about 1μm in diameter, although larger inclusions have been observed. They may be associated with thin cavities on either side.

- **Needle-shaped cavities:** These are extended narrow cavities with very small diameters of the order of 0.1μm. The lengths measured are approximately 5μm. They are generally not associated with particulate inclusions.

Heat treatment has an interesting influence on all these defects. After a treatment in the range of 1,500°C–3,000°C, the diameter of the flaw increased. It varied from 20% to 80%, while the length remained almost unchanged. Moreover, the inclusions originally visible at 1,500°C can be considerably modified. There was coalescence of distinctly separate inclusions, which then shrink. This modification of inclusions was observed to be a maximum above 200°C (13).

4. HISTORY

4.1   DISCOVERY OF CARBON FIBRES

Thomas Edison was the first to develop carbon fibres. In 1879 he invented the first incandescent light bulb, which uses electricity to heat a thin strip of material, called a filament, until it glows. To make his early filaments, Edison formed cotton threads or bamboo slivers into the proper size and shape and then baked them at high temperatures. These materials were mostly composed of cellulose, a natural polymer. When heated, the filament was "carbonized" becoming a true carbon copy of the starting material (12). The subsequent improvements in the electricity industry resulted in the development of carbon fibres on a large scale. The synthetic carbon industry had seen its official beginning in 1886 with the creation of the National Carbon Company (Cleveland, Ohio), which merged with Union Carbide in 1917 and changed its name to Union Carbide Corp. in 1957, then to GrafTech International Holdings in 2002. In 1942, the discovery of the solvent dimethylformamide (DMF) by G.H. Latham allowed the study of the structure and the properties of polyacrylonitrile (PAN). This compound became one of the most widely used precursors for carbon fibres in later years (13).

Near the end of World War II, Union Carbide started to carbonise cellulose-based polymers such as cotton. In this period, carbon fibres were still raising interest in the commercial sector. In 1957, the Barnebey-Cheney company manufactured carbon fibre based on rayon and cotton samples. This idea was taken up by Union Carbide, which in 1958 developed a carbonised rayon cloth and proposed it to the US Air Force. 1958 was also the year the high performance of these materials was discovered. Roger Bacon highlighted, thanks to his PhD's experiments within the Parma Technical Centre near Cleveland, OH, the amazing properties of carbon fibres. In fibrous forms, carbon and graphite are the strongest and stiffest materials for their weight that have ever been produced. Bacon demonstrated that carbon fibres had a tensile strength of 20 GPa and Young's modulus of 700 GPa. By comparison, steel commonly has a tensile strength of 1-2 GPa and Young's modulus of 200 GPa (12).

In 1959, Curry Ford and Charles Mitchell, two scientists at Parma Technical Centre, patented a process for making fibres by heat treating rayon at 3,000°C. They had produced the strongest commercial carbon fibres to date, which led to the entry of carbon fibres into the 'advanced composites'

industry in 1963. In 1960, Bacon was the first person to produce carbon nanotubes and published a paper in the Journal of Applied Physics. The incredible properties of these compounds have made nanotubes one of the hottest areas of research in recent years, promising to revolutionise just about every area of science (12).

The first truly high modulus commercial carbon fibres were invented in 1964, when Bacon and Wesley Schalamon made fibres from rayon using a new 'hot-stretching' process. They stretched the carbon yarn at high temperatures (more than 2,800° C), orienting the graphite layers to lie nearly parallel to the axis of the fibre. The key was to stretch the fibre as it heated, rather than after it had already reached a high temperature. The process resulted in a ten-fold increase in Young's modulus, a major step on the way to duplicating the properties of Bacon's graphite whiskers (12).

Since this discovery, carbon fibres were used to create composite components, which were manufactured at that time with fibreglass and boron fibres. Carbon fibres were much lighter, so the appearance of relatively affordable carbon composites was a welcome development, and they found widespread use in gaskets and packaging materials. The U.S. Air Force Materials Laboratory supported much of Union Carbide's research into rayon-based fibres during this period in an attempt to develop a new generation of stiff, high strength composites for rocket nozzles, missile nose tips and aircraft structures (12).

4.2   INNOVATIVE PRECURSORS

While the United States worked on rayon, Japan and England developed carbon fibres from another precursor, polyacrylonitrile (PAN). A first study performed by Akio Shindo of the Government Industrial Research Institute in Osaka (Japan) produced fibres with a modulus of more than 140 GPa, about three times that of the rayon-based fibres available at
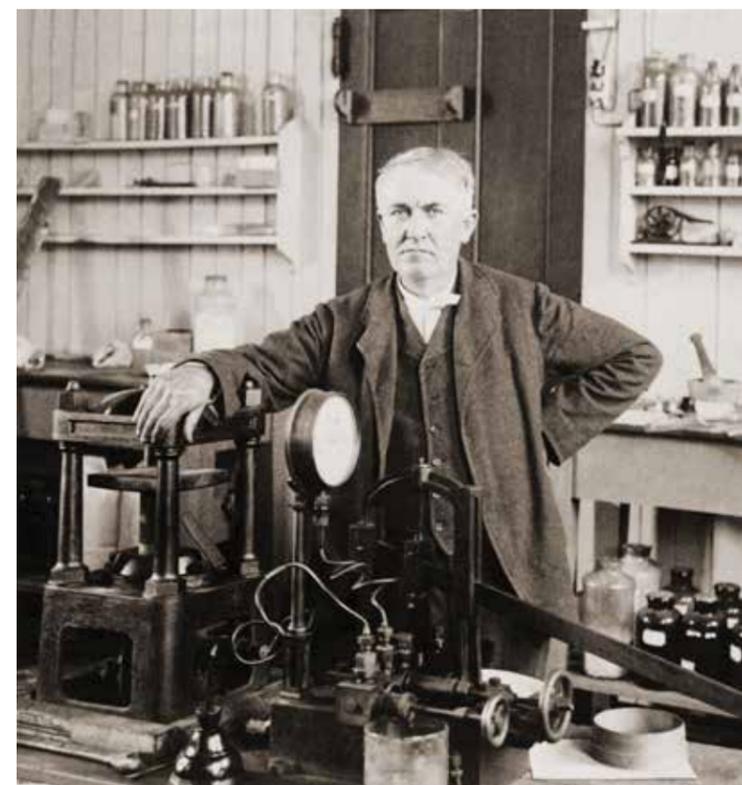
that time. Thanks to these interesting results, pilot scale production was developed in 1964. In the same period on England, the development team of William Watt and co-workers at the Royal Aircraft Establishment invented a method to stretch the PAN fibres which prevented their shrinkage during heat treatment. This important British development resulted in a fibre with much improved mechanical properties which was rapidly put into commercial production (12,13).

The step improvement achieved with the PAN can be explained by the better properties of this precursor. Its polymeric backbone and the continuous string of carbon and nitrogen atoms led to a high yield of fibres with highly oriented graphitic-like layers, eliminating the need for hot stretching. Japan's Toray Industries developed a precursor that was far superior to anything seen before, and in 1970 they signed a joint technology agreement with Union Carbide, bringing the United States back to the forefront in carbon fibre manufacture. PAN-based fibres eventually supplanted most rayon-based fibres, and they still dominate the world market (12).

PAN and rayon are both non-graphitizing materials so the carbon fibres stemming from these precursors cannot be totally graphitised, preventing further

improvements in mechanical properties. To overcome this issue, researchers found other precursors likely to be totally graphitised such as petroleum and coal-based compounds. Indeed the heating of these materials lead to the formation of a pitch — a compound possessing a very high carbon content that would form carbon fibre with a very high carbon yield, so very high performance could be observed (12).

The discovery of a mesophase, a liquid crystal state, during the formation of the pitch carbon fibre has been attributed to two Australian scientists. This finding shows how a pitch can be polymerised slightly further to orient the molecules in layered form. The orientation of the fibres can be improved by stressing the viscous mesophase to align the molecules and perform a heat treatment to convert this material to carbon fibres. This specific phase provides extremely good properties; they have an ultrahigh elastic modulus, of approximately 1,000 GPa, and also a very high thermal conductivity. However, the tensile strength is lower than that of PAN and rayon fibres (12).

Although rayon fibres were the first to be produced, they have been replaced by PAN fibres that possess higher performance. Almost 90% of the carbon fibres manufactured today are based on PAN precursor. Pitch-based fibres are unique in their ability to achieve ultrahigh Young's modulus and thermal conductivity. However, the high cost of their production process limits the use to specific domains such as niche aerospace and military applications.

5. NATURE OF PRECURSERS

5.1   INTRODUCTION

Although the majority of precursors used commercially today are PAN, rayon and pitch, several other precursors can be used to manufacture carbon fibres, including cellulosic precursors, non-heterocyclic aromatic polymers, aromatic heterocyclic polymers, linear polymers and coal. Precursors have to contain a high level of carbon atoms to create a very good cross-linked structure. The significant factors in obtaining a high carbon yield are, the nature of the polymer precursor, the nature of the degradation process, the capacity of the precursor for cyclisation, ring fusion and coalescence, and the nature of the stabilising pretreatment (13). Almost 90% of the carbon fibres currently manufactured are from PAN precursors. The other precursors that are industrialised on a large scale are rayon and mesophase pitch, due to their good properties (17).

Section of Carbon Fibre

a) Cyclisation (200-300°C)
b) Dehydration
c) Elimination of N2 (1500-2000°C)
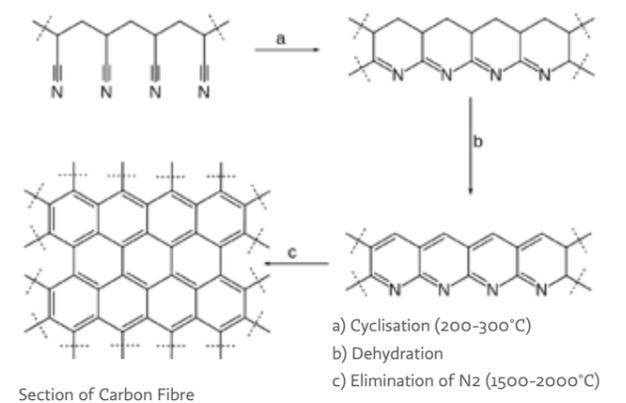
5.2   PRECURSOR TYPES

5.2.1   Polyacrylonitrile (PAN):

The exact nature of the precursor can vary depending on manufacturer, but PAN usually contains at least 85% of acrylonitrile and at most 15% of co-monomer such as methyl methacrylate, methyl acrylate, vinyl acetate, vinyl chloride and other monovinyl

Precursors	Notable Advantages	Notable Disadvantages	Remarks
PAN	• High degree of molecular orientation • Higher melting point • Greater yield of the carbon fibre (double of yield from rayon) • Good mechanical properties	Processing cost (polymerisation, spinning and coagulation, finish treatment, winding)	Large-scale production/The most used Type HM
Cellulose	Good mechanical properties	Rayon: low yield (10-30%)	Rayon: large-scale production
Pitch	• Lower material cost • •Higher char yield • Higher degree of orientation compared with PAN • Higher elastic modulus along the fibre direction • Higher thermal and electrical conductivity along the fibre direction • Synthetic: lower cost	Processing cost (purification, mesophase formation, fibre spinning)	Large-scale production Type IM
Non-heterocyclic polymer	• Easy cyclisation • Easy elimination of non-carbon atoms • Greater carbon yield (60-70%)	High cost	Tensile strength: 1,600–2,170MPa Modulus range: 350-490GPa No large scale production
Aromatic heterocyclic polymer	Anisotropic carbon fibres in good yield (>90%)	High cost	Type HM No large scale production
Linear polymer	• Suitable for melt spinning technique • High tensile strength, low modulus	• Non graphitisable • Large number of micro and transitional voids • Poor yield	Modulus: 200GPa Strength: 3GPa No large scale production
Coal	• Suitable for melt-spinning technique • Uniform diameter • Smooth external surface	• Isotropic • Very poor strength	No large scale production

Table 2 Characteristics of precursors

compounds (18). One British patent mentions the use of Courtelle, which is a ter-polymer of acrylonitrile, methyl acrylate and another vinyl monomer (19).

PAN is generally obtained by radical polymerisation of acrylonitrile. It is spun into a fibre, goes through coagulation, finish treatment and winding to obtain finished fibres of PAN. Although PAN fibres are more expensive than rayon fibres, they are extensively used as the source for carbon fibres because their carbon yield is almost double that of the carbon yield of rayon.

5.2.2   Cellulosic Precursors:

These precursors include cotton, linen, ramie, sisal, hemp and flax, however the use of regenerated cellulose or rayon is more common. Polynosic fibres have also been tried (20) but the properties were not as good as other precursors. Some investigations have focused on the mechanism of the process to try to enhance the carbon yield. Pyrolysis of cellulosic precursors in the presence of certain inorganic compounds, a modification of cellulose and also a variation of the reactive environment all showed a degree of success (21–24).

5.2.3   Pitch precursors:

Due to their high carbon yield, pitch precursors produce high performance carbon fibres. Certain fractions of asphalt and pitch were converted into carbon and graphite fibres by heat treatment, extrusion and spinning, followed by stabilisation, carbonisation and then graphitisation (25) to give carbon fibres with intermediate strength and modulus properties. Union Carbide developed a process to obtain high-modulus carbon fibres from polynuclear aromatic pitches (13). Today, most development work is focused on the production of carbon fibres from mesophase pitch (26). Some PVC-derived pitches have been tested but the heat treatment requires high-temperature stretching, which is very expensive (27).

5.2.4   Non-heterocyclic aromatic polymer precursors:

These compounds possess several advantages over other precursors in the production of carbon fibres,

indeed their cyclisation into a graphitic structure and the elimination of non-carbon atoms is very straightforward. Moreover these materials contain a high carbon yield. Many compounds have been tested such as phenolic polymers, phenol formaldehyde resin, polyacenaphtalene, polyacrylether, polyamides, polyphenylene (13, 28, 29). General Electric Co. patented a continuous method for making carbon fibres based on polyacetylene (30). The tensile strength and the modulus range of these fibres are respectively between 1,600–2,170 MPa and 350–490 GPa.

5.2.5   Aromatic heterocyclic polymers:

These polymers are generally linear and have a relatively high aromatic content. Among this class of polymers, polyimides, polybenzimidazole (31), polybenzimidazonium salt and polytriadiazoles (32) have been converted into high modulus carbon fibres. Work is currently ongoing using lignin as a precursor, which will conform to many of the sustainability requirements that are now of particular interest (33).

5.2.6   Linear polymers:

Some investigations have been made on certain linear thermoplastic polymers but led to the production of carbon fibres with poor mechanical properties (low modulus and low strength). A mix of polyethylene and polypropylene (34), polyvinyl chloride (35), poly vinyl ketone are examples of polymers used as precursors. These types of fibres are generally non-graphitisable and contain a large number of voids leading to poor mechanical properties.

5.2.7   Coal

Carbon fibres have been prepared from certain coal extracts obtained by digesting coal at elevated temperatures and under high pressures with high-boiling aromatic solvent. These fibres are known to be isotropic and possess a very poor strength (36).

5.3   PROPERTIES OF PRECURSORS

Each precursor brings specific characteristics to the carbon fibres. The table below shows some advantages and drawbacks linked to the nature of the precursors (Table 2).precursors (Table 2).

6. MANUFACTURE OF CARBON FIBRES

6.1 PROCESS

The technique to manufacture carbon fibres is quite similar for every precursor. The steps are stabilisation, carbonisation, then graphitisation. Each step is essential to obtain carbon fibres with very good performance.

a) Heat stabilisation:

The heat stabilisation is made at temperatures between 200–300°C and generally in air for between 30 minutes and three hours. This step, involving oxidation, is essential to prevent melting or fusion of fibres, it alters spun fibres at the atomic level, breaking hydrogen bonds and picking up oxygen molecules. Moreover a stretching process is sometimes accomplished in the same time to increase the mechanical properties of the fibres (12, 17).

b) Carbonisation:

Carbonisation is a heat treatment at high temperature (1,000°C–1,500°C) involving the elimination of the non-carbon elements. This process, performed in an inert atmosphere (often diazote), is very quick (a few minutes). The heating rate is very slow to prevent damaging the fibres. This step is not accomplished under tension. At the end of this process, the product is composed of approximately 90% carbon, 8–9% azote, 1% oxygen and less than 1% hydrogen. This structure possesses a high resistance and, on average, a high Young modulus (3,000-6,000MPa). This last parameter can be improved by a last step, graphitisation; however, carbon fibres can be used without this process. In fact, some applications required carbonised fibres with only a finishing treatment such as a coating (14).

c) Graphitisation:

Graphitisation is an optional step but it is usually undertaken because of the good properties obtained at the end of the process. Fibres are exposed for a few seconds to a temperature of between 2,000°C and 3,000°C to allow graphitisation. During this process, the more or less pre-ordered carbon is converted into a three-dimensionally ordered graphite structure. Depending on the raw materials and the processing parameters, various degrees of convergence to the ideal structure of a graphite single crystal are achieved (37).

The chemical bonds present in the 1–2 plane are sp2 bonds. This kind of bonding links together carbon atoms present into the cycles causing a very strong assembly. These connections involve very good mechanical properties into the 1–2 planes. However, the bonds present between the planes are relatively weak Van der Waals bonds. At the end of this route, the fibre is composed of almost 99% carbon. The stretching step during this process is optional but improves the elastic properties significantly (14).

d) Surface treatment:

To enhance the mechanical properties of the final carbon fibres, some surface treatments are performed. This step allows a better adhesion between the fibres and the matrix during the manufacture of the composite prepreg (14). The interfacial bond between the carbon filament and the resin matrix material can be enhanced either by enlarging the surface area, which provides more points of contact between the fibre and the matrix, or by enhancing the chemical interaction between the two. Two kinds of treatments are generally performed: oxidative treatments such as gas-phase oxidations at lower or at higher temperatures; liquid-phase oxidations carried out chemically or electro-chemically; or catalytic oxidations and non-oxidative treatments such as whiskerisation, deposition of pyrolitic carbon, or grafting of polymers on surface (13).

6.2 MANUFACTURING CARBON FIBRE FROM PAN

The manufacturing process for PAN carbon fibres is similar to that of the other precursors and comprises the three steps described previously.

The oxidation taking place during the first stage allows the conversion of thermoplastic PAN into a non-plastic cyclic or ladder compound capable of withstanding high temperature. This step is essential so as not to destroy the fibres during the carbonisation step. PAN is usually composed of 85% acrylonitrile and 15% co-monomer, generally methyl acrylate. This compound acts as a plasticiser to aid the spinning process and put the polyacrylonitrile in a wire form. Moreover it also helps the stretching of the fibre during the oxidation treatment. Air plays an important role during the heat treatment because it promotes the initiation of cyclisation by forming activated centres. It is responsible for the increased number of activated centres and it minimizes any parasitic reactions (13).

The nitrile group, having a high polar character, causes strong dipole-dipole forces that act as crosslinks. This kind of interaction increases the polymers' solubility to highly ionizing solvents, increases its melting point and makes it more suitable as a carbon fibre precursor. However, these forces prevent necessary rearrangements for the development of crystallinity and cause shrinkage of the fibre on heat treatment. This problem has been observed by Shindo (38), who reported obtaining poor mechanical properties with these types of fibres. Johnson and co-workers (39) overcame this issue by stretching the fibre on a frame; the resulting carbon fibres had better mechanical properties (13). Oxidation of PAN fibres has been the subject of numerous investigations and several different structures have been proposed for the cyclised PAN material.

One variant solution, which includes performing the oxidation under a flow of SO2 has been tested by Raskovic et al (40). The use of this gas results in the incorporation of a considerable amount of sulphur into the fibre chemical structure. This compound forms bridges resulting in a very rigid chemical structure and the process combines two temperature zones to encourage better crosslinking and a higher initial carbon content. The resulting mechanical properties are good (13).

The second stage is the carbonisation of the fibres. This pyrolysis process is essential to remove the organic compounds. At the end of this heating, only carbon and some nitrogen are left. A low heating rate is required to avoid damaging the fibres by the release of volatiles. This thermal treatment is composed of two stages, dehydrogenation and denitrogenation. Hydrogen is removed, involving the reorganisation and a coalescence of the cyclised sections. Then nitrogen is eliminated at high temperature to create a structure highly rich in carbon.

Graphitisation (Stage 3) aims to improve the ordering and the orientation of the crystallites in the direction of the fibre axis. This results in better mechanical properties of the final carbon fibre (13). Molecules tend to align themselves in the same direction. The restructuring creates very strong bonds in the planes of the molecules.

6.3 MANUFACTURING CARBON FIBRES FROM RAYON

Rayon is manufactured with regenerated cellulose fibre. Because it is produced from naturally occurring polymers, it is neither a truly synthetic fibre nor a natural fibre; it is a semi-synthetic (41) or artificial fibre. Cellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand D-glucose units (42). The transformation of cellulose in rayon is performed according to the following steps (43) (Figure 2):

1. **Immersion:** cellulose is dissolved in caustic soda (NaOH).

2. **Pressing:** removal of the excess of liquid.

3. **White crumb:** the pressed sheets are crumbled or shredded to produce what is known as "white crumb".

4. **Aging:** exposure of the "white crumb" to oxygen.

5. **Xanthation:** formation of cellulose xanthate by exposure of "white crumb" to carbon disulfite (CS2), reaction accomplished in vats and under controlled temperature (20 to 30°C).

6. **Yellow crumb:** Xanthation changes the chemical makeup of the cellulose mixture and the resulting product is now called "yellow crumb".
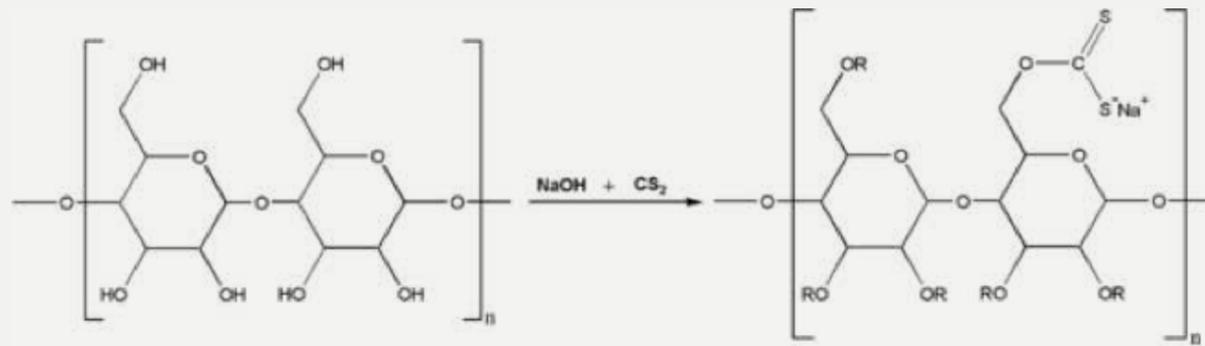
Figure 2 Chemical formation of rayon.

7. **Viscose:** dissolution of "yellow crumb" in a caustic solution to form viscose.

8. **Ripening:** viscose is set to stand for a period of time $(C6H9O4O-SC-SNa)n + nH2O$ ⇌ $(C6H10O5)n + nCS2 + nNaOH$.

9. **Filtering:** removal of the undissolved particles.

10. **Degassing:** any bubbles of air are pressed in a degassing process.

11. **Extruding:** extrusion of the viscose by a spinneret.

12. **Acid bath:** viscose is placed in a bath of sulphuric acid, resulting in the formation of rayon filaments $(C6H9O4O-SC-SNa)n + ½nH2SO4$ ⇌ $(C6H10O5)n + nCS2 + ½nNa2SO4$

13. **Drawing:** stretching of the rayon filament to straighten out the fibres.

14. **Washing:** removal of any residual chemicals.

15. **Cutting:** the filaments are cut down when producing staple fibres.

The steps of rayon-based carbon fibre manufacture are similar to those used to make PAN-based carbon fibre; i.e. stabilisation, carbonisation and graphitisation stages. For rayon based fibres, during the stabilisation process, four phases occur. A physical desorption of water is initiated between 25°C and 150°C, then a dehydration of the cellulosic unit takes place and finally a thermal cleavage of the cyclosidic linkage and scission of ether bonds and some C-C bonds via a free radical reaction (240–400°C) occur and then aromatisation follows. The carbonisation of these fibres is accomplished between 400°C and 700°C, and the structure is converted into graphite-like layers. Graphitisation is carried out usually under strain at between 700°C and 2,700°C to obtain a high modulus fibre through longitudinal orientation of the planes (43).

Several processes are possible in the production of rayon based carbon fibre. The first one is the use of temperature increasing with a slow rate to allow the complete conversion. This technique involves the dehydration of the products and provides a high yield of carbon fibre. However, this method requires a high quantity of energy. To reduce costs, another solution uses a reactive atmosphere such as air, oxygen, chlorine or HCl vapor. This technique promotes dehydration of cellulose and inhibits the formation of tar. The presence of hydrogen bonds can give rise to a highly cross-linked intermediate resulting in a better carbon yield. The processing time and the carbon yield vary with the nature of the

reactive atmosphere. The time of processing varies between 20 minutes and 10 hours, and the carbon yield for rayon carbonised up to 1,000°C varied from 23% in air or oxygen atmospheres, to 27% in a chlorine atmosphere, to 35% in HCl vapor (22, 24 and 44). This method, although providing a good carbon yield and a decrease in the energy requirement, is limited by the rate of diffusion of reactive gas species into the interior of the fibre involving a relatively slow process. The last solution involves the use of flame retardant, which impregnates the fibres with an aqueous solution of nitrogenous salts and certain phosphoric esters before the heat treatment (45). The presence of the flame retardant allows the increase of the amount of carbon descended from cellulose to remain in the fibre. The flame retardant either catalyses a reaction involving the elimination of hydroxyl groups or reacts with the hydroxyl group and promotes dehydration of the cellulose material at low temperature. The pyrolysis of rayon in the presence of flame retardants produces dehydrocellulose exclusive of levoglucosen. A weight loss of up to 200°C was found, due exclusively to the volatilisation of water, and no carbon-containing gases were detected. This phenomenon explains the good yield of carbon obtained. Moreover, this technique is more economical thanks to the use of a lower temperature and a faster rate reaction.

The exact stage where the carbonisation has to be performed can be detected using infrared spectral analysis. In fact, between 240°C and 400°C only minor changes in C=O bonds and no changes in C=C bonds occur. Above 400°C the C-H and C=O bonds became weak, and the incidence of C=O bonds diminished further if temperature is increased. In the case of rayon-based carbon fibres, carbonisation is accomplished at 1,000–1,500°C under inert atmosphere, and stretching can also be achieved during this step to enhance the mechanical properties (46).

One study describing X-ray analysis demonstrated that the graphitised layers are formed with the orientation in the direction of the original cellulose chain. However, another work showed that the natural orientation of the fibre was almost completely lost during the carbonisation (47–48). Thus the ultimate orientation cannot be adequate unless graphitisation is carried out under stress. Usually the temperature during this process was above 2,800°C for a fraction of a second under stress. The Young's modulus of the fibre was generally found to be directly related to the graphitisation temperature and the amount of stretch applied (22).

6.4 MANUFACTURING CARBON FIBRES FROM PITCH

Pitch is the second most widely used precursor worldwide. It is available in large quantities for lower costs than the other precursors and it produces high performance carbon fibres. However, the purification and the spinning steps increase the costs of manufacturing. In 1990, the most commonly used pitches were those made from petroleum, asphalt, coal tar and PVC. The composition varied with the source and the processing conditions, for instance coal pitch is generally more aromatic than petroleum pitch. A study reported that coal tar is composed of 2/3 of aromatics compounds (49). However coal pitch often has a high carbon particle content, which causes filament breakage during extrusion and thermal treatment. Therefore petroleum pitch is preferred for carbon fibre production (50).

The main issue with this kind of fibre is their isotropic behaviour before pyrolysis. This phenomenon prevents the formation of oriented carbon fibres. Two solutions have been proposed: graphitisation under stress or the use of mesophase pitch. The first solution is carried out under tension during heat treatment at high temperature, between 2,000°C and 3,000°C. This technique provides carbon fibres with excellent performance properties but is very expensive. That is why the second solution is preferred. Mesophase is a state of matter intermediate between liquid and solid, and this process allows the conversion of crystallised material into fibres. This state permits the orientation of the lamellar structure in the fibre in a low-temperature spinning operation.

The fabrication of this kind of fibre consists of four steps:

1) Pitch preparation

2) Spinning, drawing

3) Stabilisation

4) Carbonisation, graphitisation

The pitch preparation stage involves an adjustment in the molecular weight, viscosity and crystal orientation for spinning and further heating. Spinning and drawing convert the pitch into filaments with some alignment in the crystallites to achieve the directional characteristics (13). Pitches are thermoplastic in nature. However, they are able to be converted to a non-fusible state. This transformation is performed during the stabilisation step, between 250°C and 400°C. The properties of these carbon fibres are largely dependent on their chemical decomposition and molecular weight distribution of the precursor. This last parameter plays a very important role during the production of carbon fibres. It determines the temperature and the speed of spinning by controlling the viscosity of the melt and the melting range. These parameters can be controlled by the addition of certain substances such as tetramethyl thiuram, polymers (such as polyethylene and polystyrene), plasticisers (such as castor oil or alkylated and sulphided derivatives) (51, 52), by extraction with certain solvents (53) or by distillation (54). The steps of carbonisation and graphitisation are performed between 1,000°C and 2,500°C.

6.5 MESOPHASE PITCH

Mesophase pitch is the best alternative to avoid the isotropic behaviour of the pitch known currently. This phase orients itself along the fibre axis direction during the precursor fibre spinning (50). This product contains an appreciable amount of anisotropic phase (liquid crystalline phase) and an isotropic phase; the two phases are melt spinnable. This kind of pitch is prepared by thermal treatment of small poly-nuclear aromatics, present in coal, or by by-products of the

thermal cracking of petroleum fractions or of certain crudes. The aromatic compounds of molecular weight of 400-600 are heated between 350°C and 500°C in an inert atmosphere for prolonged periods (days to hours). The molecules undergo a succession of dehydrogenative condensation reactions, forming large molecules that aggregate into a liquid crystalline phase with a nematic order. This phase, called mesophase, has a higher surface tension than the low-molecular-weight isotropic liquid phase and coalescence into larger spheres is observed, as the anisotropic regions extend.

The process parameters of the mesophase formation are crucial. The increase in the mesophase concentration involves a rise in the viscosity of this mixture of phases, requiring a higher temperature for spinning. This higher temperature is beneficial because it allows a higher carbon yield. However, this parameter can be a problem if the amount of mesophase reaches 50%. A phase inversion occurs and the anisotropic phase becomes continuous and surrounds the spherules in the remaining isotropic material. With a high temperature, mesophase polymerises and solidifies into coke. This solidification must be avoided in the production of carbon fibres. Moreover, the molecular weight of the mesophase spherules increases with the coalescence resulting from sedimentation of this phase. To avoid this issue, several techniques are used including agitation during pyrolysis (56) or a decrease of the pyrolysis temperature in the range of 380°C–410°C (57). Some studies demonstrated that a step of solvent extraction during the formation of mesophase, or vacuum stripping were beneficial to the fabrication of carbon fibres (58–59).

The mechanism of the formation of graphitised fibres starts with the formation of molecular stacks and micro-domain units from aromatic planar molecules in the liquid crystal mesophase pitch. Then the system is spun to allow the alignment of the micro-domains. Finally, the graphitisation of the fibres occurs.

Union carbide patented a method to form mesophase pitch with petroleum pitch heated to 360–400°C

for 12–24 hours under a nitrogen atmosphere and in constant agitation to avoid sedimentation. Then condensation occurred and fibres were spun at 370°–400°C. To reduce fibre sticking and fusion during the heat stabilisation treatment, the scientists applied colloidal graphite or an aqueous suspension of carbon black in ammonium 2-ethylhexyl sulphate on the surface before stretching and winding (60).

Another patent, written by Exxon Research and Engineering, described the formation of mesophase pitch based on petroleum pitch Ashland A-240 and A-260. High-molecular-weight components tend to form coke during heating so the removal of these components is essential to create carbon fibres with an acceptable yield. In the first step, the precursor pitch was extracted with toluene to remove these components. The solvent-insoluble fraction, called the neomesophase former, softens between 230°C and 400°C, producing mesophase. As the neomesophase has a lower softening point than that of the mesophase, it can be spun at a lower temperature, thus reducing the formation of coke during heating and spinning. In the Exxon work, the precursor was vacuum stripped at 420°C, cooled at room temperature and then extracted to separate the insoluble neomesophase. Although this technique reduces the formation of coke, it provides a smaller quantity of carbon fibres than the Union Carbide method (59).

Another route, patented by Kyushu Industrial Research Institute, involves the formation of mesophase pitch by hydrogenation using a hydrogen donor solvent such as tetrahydroquinoline. An optional step before the hydrogenation consists of de-ashing and distilling the system. After the hydrogenation, the product was filtered and heated to remove low-volatile contents and produce mesophase. Then spinning occurred as usual (61). Otani patented a similar method to the Kyushu Industrial Research Institute, except for the absence of solvent.

As explained previously, spinning can be difficult due to several parameters such as the sedimentation of

the mesophase; the transition of the mesophase; the transformation of high-molecular weight compounds into coke; the high viscosity of the mesophase; and the presence of gas bubbles, which can produce defects in the final fibre. Currently the techniques used are centrifugal spinning, jet spinning and conventional melt spinning, and the important parameters to control are spinning temperature, pitch temperature, mesophase content in the pitch, filament speed (≈2.5m/sec), diameter of the filament, ratio length and diameter of the spinneret, and draw ratio (13).

As mesophase pitches have higher softening points, the oxidation treatment can be carried out at a higher temperature, where diffusion and oxidation processes are faster. The stabilisation occurs usually between 250°C and 350°C in electrically heated air ovens for about 40 minutes. Then carbonisation eliminates any remaining heteroatoms and helps in the development of a larger structure. The process takes place at 700–900°C for a few minutes to remove the volatiles and to avoid excessive disruption. Finally, graphitisation improves the carbon fibres further by heat treatment between 2,500–3,000°C. A study demonstrated that when the graphitisation takes place after heat treatment at 3,000°C the Young's modulus approaches a value of 886GPa, close to the graphite single-crystal value of 1,000GPa (62).

7.   INNOVATION

7.1   NEW PROCESSES

Carbon fibres are high performance materials widely used in many fields thanks to their specific properties. Therefore research and development in this field is very active and one major driver is cost reduction. In 2014, another priority has been sustainability, towards the development of carbon fibres produced with biomaterials such as lignin, chitosan, etc. and the development of new processes requiring less energy such as microwave or plasma. Several patents describe some techniques to produce carbon fibres with lignin using several possible processes (63-66). In 2010, an innovative process to produce carbon fibre using microwave-assisted plasma (MAP) appeared (67) at the Oak Ridge National Laboratory, Tennessee. This invention involves an elongated chamber in which a microwave plasma is excited in a selected gas atmosphere. Fibre is drawn continuously through the chamber, entering and exiting through openings designed to minimize in-leakage of air. A gradient of microwave power is set up to avoid damage to the fibres. This technique is suitable for all kinds of precursors such as PAN, pitch, and mixed organic/polymeric precursors. Oxidized or partially oxidized precursors are run continuously through a MAP reactor in an inert and non-oxidizing atmosphere to heat the fibres; drive off the unwanted elements such as oxygen, nitrogen and hydrogen; and produce

carbon or graphite fibres faster than conventionally produced carbon fibres (65).

In one attempt to encourage the development of new low cost sustainable carbon fibres, the Oak Ridge National Laboratory has commissioned a new carbon fibre technology facility for the US energy sector. Companies are being invited to suggest new candidate precursors for the novel, low cost production of carbon fibres (67).

The US Department of Energy (DoE) awarded a total of $11.3m in 2014 to fund two projects, one with the Southern Research Institute of Birmingham (Alabama) to convert sugars from non-food biomass to acrylonitrile, and the other with the National Renewable Energy Laboratory (NREL) in Colorado, to optimise pathways to acrylonitrile using lignin enriched biomass (68).

In addition, the European Union called for proposals to develop new precursors, processing routes and functionalisations for carbon fibres in 2013 (69). This call generated projects that commenced in 2014, including FIBRALSPEC (70) — developing fibres based on the precursors silicon carbide, textile-grade PAN, polyolefins, and lignin, in addition to a new environmentally friendly pitch, obtained from anthracene oil, for the preparation of isotropic carbon fibres. The same call also produced project NEWSPEC

(71), which is developing carbon fibres from the precursors recycled polyethylene, bio-ethanol and synthetic oil; and project CARBOPREC (72), where the precursors are based on lignin and cellulose with carbon nanotube reinforcements.

In anticipation to increased demand in carbon fibres for thermoplastic matrix composites, SGL has developed a size especially for a range of thermoplastics to be applied in the automotive sector (73).

7.2   RECYCLING

The development of new technologies and, in particular, composites, allows the aerospace and automotive sectors to improve continuously by decreasing the weight of their structures. Today, composites make up a high proportion of the structure of an aircraft — in fact, approximately 50% by weight in the latest generation (B787, A350 XWB, JSF, etc.) and there are strong predictions that it will rise still further. When thousands of largely composite aircraft reach the ends of their 25–30 year service lives, end of life disposal will become a serious problem if effective recycling systems are not developed (74). In the automotive sector, with the increasing use of carbon fibres, recycling will also be increasingly important to conform to end-of-life vehicle requirements.

Currently the end-of-life materials are sent to landfill or incinerated and only a small proportion of composites are reused. However, neither landfill nor incineration disposal of CFRP is optimal. Several studies have been performed to find methods to improve the overall properties of reclaimed fibres and to improve the processing of these materials, and two very useful reviews are provided by Pickering (75) and Job (76).

a)   Pyrolysis:

The technique currently most used is pyrolysis, with or without the aid of a catalyst. Composites are placed in an oven in the absence of air and at a temperature of between 400°C–500°C. This process cleans the carbon fibres and they maintain 90–95% of their original properties. Several companies use

this innovative technique such as Recycled Carbon Fibre Ltd. (now ELG Carbon Fibre, West Midlands, UK) and the Recycling Committee of the Japan Carbon Fibre Manufacturers Association (JCMA) — which includes Toray Industries Inc. (Tokyo, Japan), Toho Tenax Co. (Tokyo, Japan), Mitsubishi Rayon Co. (Osaka, Japan), Hadeg Recycling GmbH (Germany), CFK Valley Recycling GmbH (Germany), Boeing and Alenia Aeronautica (Rome, Italy). RCF (www. recycledcarbonfibre.com), one of the foremost companies of recycling currently, possesses a highly sophisticated 37m long pyrolysis machine, reportedly capable of recycling approximately 2,000 metric tonnes of waste material per year (77).

b)   Fluidised bed

In the fluidised bed process, crushed composite scrap material is fed into a bed of sand and a stream of fluid (for example a gaseous airstream) is forced through the material at a temperature of 550°C. Organic material, including the composite's resin matrix and any contaminants, is oxidised. However, the velocity of the airflow is such that as the organics burn off and the lightweight fibre is forced upwards, while the heavier matter, such as metallic material, remains in the reactor 'bed'. Carbon fibres processed through the fluidised bed at 550°C showed a strength degradation of 20% and the original stiffness of the fibre was retained. In addition, an analysis of the surface after recycling showed only a small reduction in oxygen content, indicating good bondability to a polymeric matrix if reused in a composite application (75).

c)   Microwave:

New technologies such as microwave or supercritical fluids have been developed and studied more recently. Microwave energy absorbed by the carbon fibres heats the matrix resin internally rather than externally. It can result in a more rapid resin decomposition and recovery of fibres without the formation of char, and shorter overall processing time. It requires smaller-scale equipment than other pyrolysis methods (78). A continuous microwave recycling method has been developed by Firebird Advanced Materials Inc. (Raleigh, N.C.).

d) Supercritical fluids:

A team at the University of Nottingham (UK) has led studies into the use of supercritical fluids, such as n-propanol, to recycle composites to enable the collection of pure PAN-based carbon fibres at the end of the process. The reclaimed fibres reportedly retain up to 97% of the tensile strength of the virgin material, with no change in modulus (79). However, the surface oxygen concentration was slightly reduced, indicating a probable reduction of interfacial strength with polymeric matrix materials in any potential reuse in composite applications.

e) Combination of methods:

The Massachusetts Institute of Technology (MIT) produced a technique combining dry and wet processes. Low temperature was used to remove the bulk matrix and some contaminants, followed by thermal post-treatment through vacuum pyrolysis to eliminate any remaining resin and produce 99% fibre purity. An innovative method has been developed by Adherent Technologies Inc., ATI (Albuquerque, N.M.), which combines three methods: vacuum pyrolysis, a dry process operated at around 500°C and the recovery of resins as marketable liquids (80). ATI demonstrated that the combination of a low-temperature (150°C) wet process and the vacuum pyrolysis could remove 23kg of insoluble contaminants per hour. This process was efficient but required customised equipment and is currently not considered optimal for commercial recycling production (78). The University of Manchester calculated the energy efficiency and environmental impact of milling carbon fibre composites as a recycling technology (81).
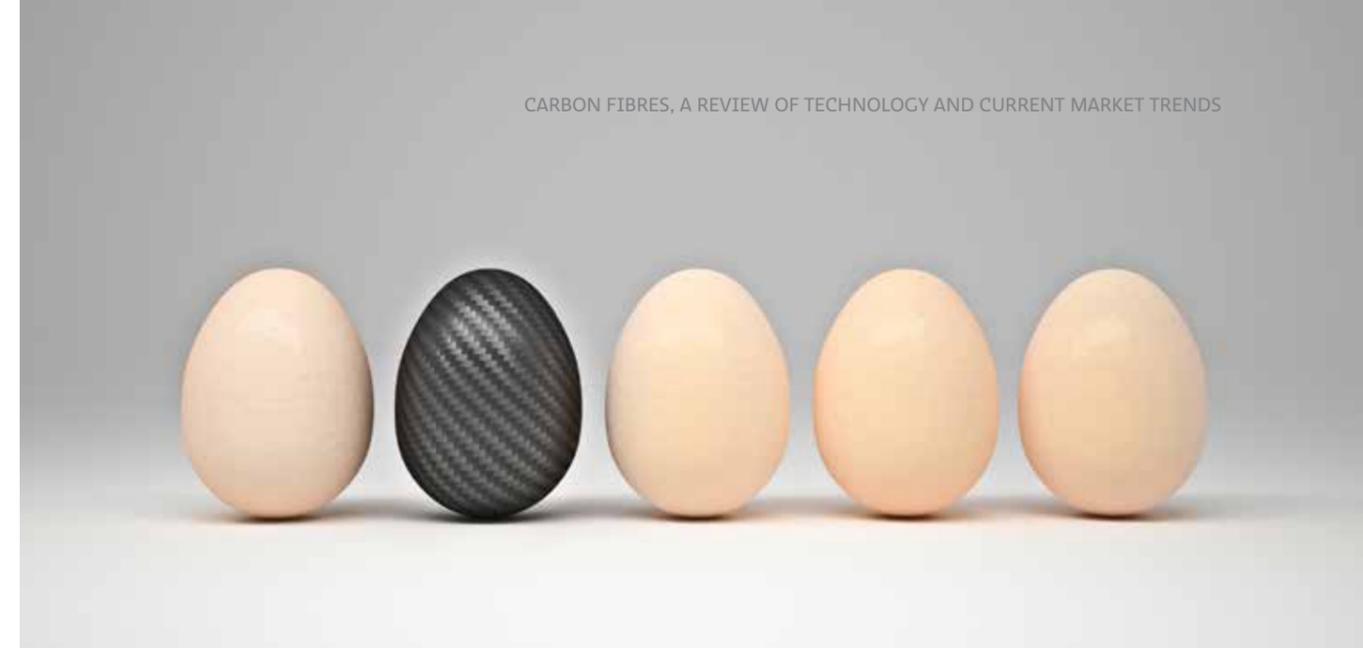
8. CONCLUSIONS

Carbon fibres are being constantly improved to reduce costs, optimise production methods and enhance performance. Today they are used in almost all sectors of industry and the growth in the wind, aerospace and offshore sectors assures their future for many years to come.

The following conclusions can be drawn:

- The markets for carbon fibres are expanding and they are as large today as they have ever been.

- The automotive sector is strongly interested in carbon fibres and manufacturers including BMW are using carbon fibres in volume production.

- There is much research going into the development of precursors for carbon fibre to refine existing precursors to improve fibre quality, to reduce the cost of carbon fibre manufacture, and to develop precursors from sustainable chemical and biological sources.

- Research and development into recycling technologies for carbon fibres is producing some promising candidates, including fluidised bed and microwave recycling.

This review has provided a top-level view of the markets for carbon fibres and their immediately foreseeable dynamics, together with areas for particular growth. The properties of carbon fibres have been summarised, together with their common defects in the context of manufacture and quality. The production processes for carbon fibres have been reviewed, including the history of the development of these technologies. In this context, recent innovations have been reviewed and predictions have been made for the next developments in production technology.

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