

Chapter 1

History and Structure of Carbon Fibers

Soo-Jin Park and Seul-Yi Lee

Abstract In this chapter, we will introduce the brief overview of carbon fibers showing superior performance and comprising expensive materials. Further, the origin and history, definition and classification, manufacturing technology, and world market and industry trends in carbon fibers will be presented. Recently, carbon fibers have attracted attention for their potential use as structural materials in aerospace, sports, cars, and bridges. Also, carbon fibers have been considered as the next-generation materials in the aerospace/aviation industry, which has presented a huge opportunity to the entire supply chain of carbon fibers.

1.1 Introduction

Carbon has a number of distinct molecular or crystalline forms termed as allotropes. These carbon allotropes have distinct properties, which are derived from their unique structures. The two most notable allotropes of carbon, each containing an infinite network, are diamond and graphite. These two solids share the same chemistry (carbon) but possess different structures and properties. For example, diamond is the hardest known material, while graphite is extremely soft.

Diamond is the perfect atomic crystal of a giant molecule. It is comprised of sp^3 hybridized carbon atoms joined by four strong covalent bonds (each 0.154 nm long) with complete electron pairs, as typically found in covalent molecules. As shown in Fig. 1.1, the other four carbon atoms point toward the corners of a regular tetrahedron to form a strongly bonded covalent structure. Diamond has three major crystal forms: cubic (100 plane), dodecahedral (110 plane), and octahedral forms (111 plane) (Fig. 1.2) [1].

Graphite is a layered structure with hexagonally arranged carbon atoms in a planar condensed ring system. It has three 0.1415-nm-long strong bonds within the

S.-J. Park (✉) · S.-Y. Lee
Department of Chemistry, Inha University, 100 Inharo, Incheon, Republic of Korea
e-mail: sjpark@inha.ac.kr

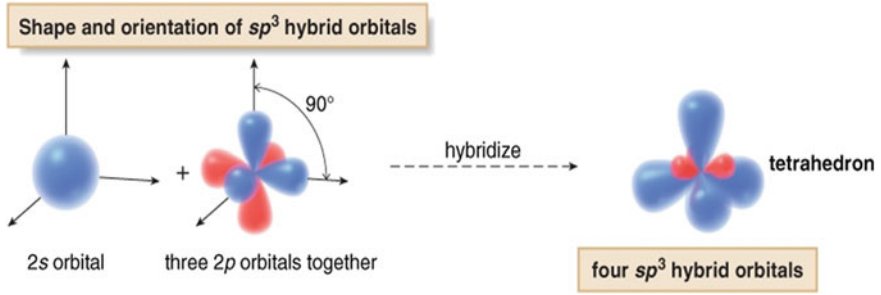


Fig. 1.1 Shape and orientation of sp^3 hybridized orbitals

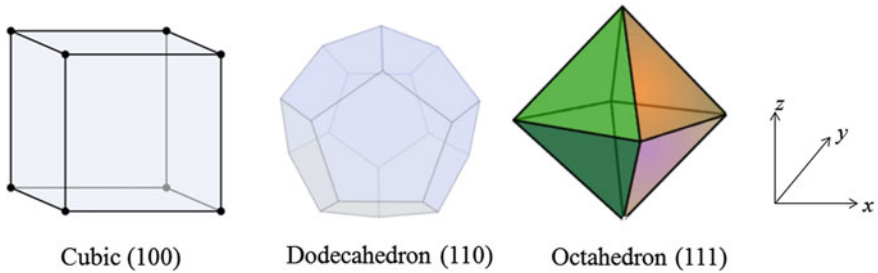
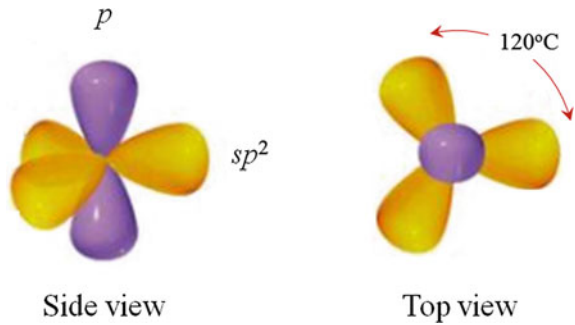


Fig. 1.2 Major crystal forms of diamond

Fig. 1.3 Shape and orientation of sp^2 hybridized orbitals



layer that are sp^2 hybridized with one electron capable of taking on a dual role, i.e., formation of coplanar and interplanar bondings, as shown in Fig. 1.3. These distributions are called “ π ” and “ σ ” distributions, respectively. The graphite layers are weakly bonded through van der Waal forces. In 1985, a new true carbon form having both sp^2 and sp^3 hybridizations was discovered and was named “fullerenes” [2].

The relationship among the different allotropes of carbon is presented in Fig. 1.4.

In addition, there are fibrous forms of carbon such as pyrolytic graphite [3], glass-like carbon [4], graphite whiskers [5], vapor-grown carbon fibers (VGCF) and catalytic chemical vapor-deposited filaments [6–9], and carbon fibers [10]. Some

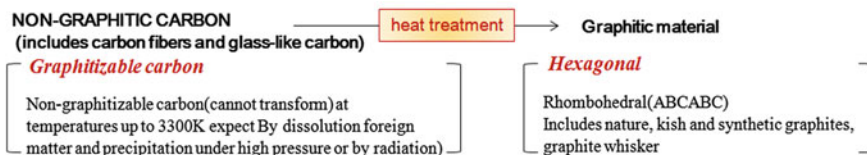
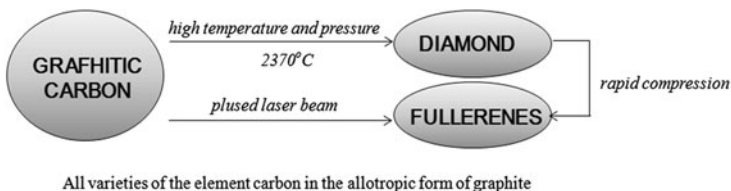


Fig. 1.4 Relationship among the allotropes of carbon

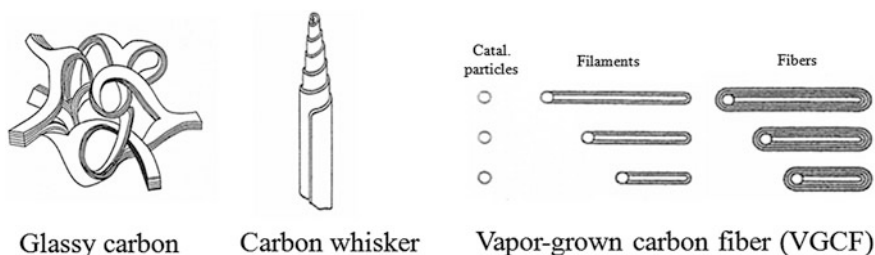


Fig. 1.5 Fibrous forms of carbon

other forms of carbon are carbon black, charcoal, coal, coke, and soot [11]. Finally, the newer forms of carbon are fullerenes [12], carbon nanotubes [13], and graphene [14] (Figs. 1.5 and 1.6).

1.2 Origin and History of Carbon Fibers

The earliest known commercial use of carbon fibers was in the carbonization of cotton and bamboo fibers for incandescent lamp filaments. In 1879, Thomas Alva Edison, for the first time, used carbon fiber filaments (testing materials) in his early incandescent light bulb experiments, which used electricity to heat a thin strip of material, called a filament, until it glowed. Later, carbon fibers were discovered in 1880, and he patented the use of carbon fibers as filament materials for his electric lamp [15]. Also, he might have created the first commercial carbon fibers. The carbon fibers that Edison made using the natural bamboo fibers or cotton threads were fire resistant, making them ideal for his early incandescent filaments. Cotton and bamboo mostly consist of cellulose, a natural linear polymer composed of



Fig. 1.6 Various types of carbon

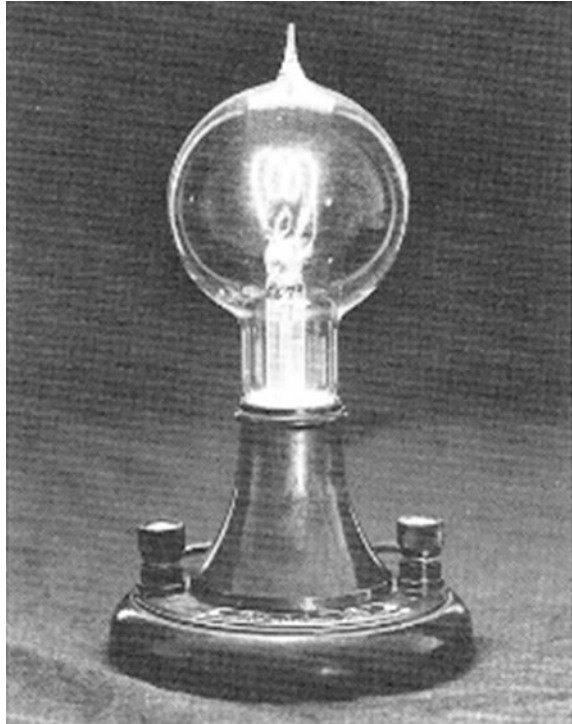
repeating units of glucose. When heated, the filament carbonized in the absence of air in a heated gas furnace and then formed a true carbon copy of the starting materials with exact sizes or shapes. Meanwhile, the use of carbon filaments for electric lamps was relatively short-lived; tungsten wire soon displaced these carbon filaments. However, the carbon filaments were in use on US Navy ships as late as 1960 because they withstood ship vibrations better than tungsten (Fig. 1.7).

The carbon fibers were first employed by Edison as a filament material in the initial development of the electric light, and that paved the way for the use of more efficient and durable materials within a few years. In particular, the fibrous nature turned out to be of great importance for structural developments in the aerospace and automotive fields. It was expected that the carbon fibers would substitute glass fibers in several fields, including transportation, building construction, marine, electrical and thermal insulation, and industrial products.

The practical commercial uses of carbon fibers, such as reinforcement, came into being since the 1960s when it became apparent that the carbon fibers, which contributed significantly to the strength and stiffness of structural products, could be developed.

The Union Carbide Corporation (UCC) during World War II investigated the fabricated carbon fibers analogously to manufacture rayon and polyacrylonitrile (PAN). Two manufacturing processes high-strength and high-modulus carbon fibers from rayon and PAN precursor fibers were simultaneously developed in 1959 and 1962, respectively. In 1963, the pitch-derived carbon fibers, with high-modulus properties, were invented. Until now, many precursor materials such as polyesters, polyamides, polyvinyl alcohol, polyvinylidene, poly-p-phenylene, and phenolic resins have been investigated for manufacturing carbon fibers [16–32]. The invention of carbon filaments by Edison paved the way for the oriented process, which was developed nearly a century later to produce the carbon fibers from synthetic fibers.

Fig. 1.7 Replica of Edison's first electric lamp containing a carbon fiber filament [15]



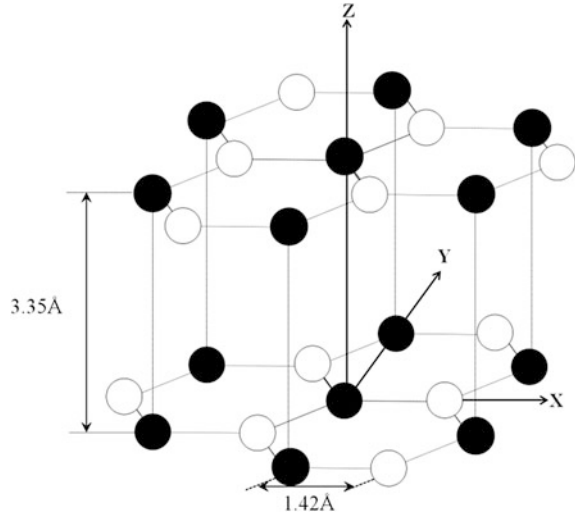
1.3 Definition of Carbon Fibers

Historically, a distinction was made between the fibers, which were heat-treated over the range 1,000–1,500 °C, called carbon fibers, and those heat-treated above 2,000 °C, called graphite fibers. The proportion of graphite in carbon fibers could range from 0 to 100 %. When the proportion was above 99 %, the fibers were called graphite fibers.

Generally, carbon fibers are widely defined as fibers containing at least 92 and up to 100 wt% carbon. Moreover, carbon fibers are polycrystalline, and usually in the nongraphitic stage. They possess a two-dimensional long-range order of carbon atoms in planar hexagonal networks (Fig. 1.8), but without any measurable crystallographic order in the third direction (z -direction) apart from more or less parallel stacking [33, 34].

On the other hand, a graphite whisker (or carbon whisker) is a single crystal with the carbon layer rolled up like a scroll. The TEM observations of graphite whiskers are presented in Fig. 1.9 [35]. Because of the single crystal nature, graphite whiskers are virtually flaw-free and have exceptionally high strength. However, the production yield of graphite whiskers is too low to be commercially significant [35, 36].

Fig. 1.8 Crystal structure of graphite



1.4 Classification of Carbon Fibers

The carbon fibers play a crucial role in a variety of specialized applications such as aerospace, automobiles, chemical industry, general engineering, missiles, nuclear energy, reinforcement in composite materials, and textiles, owing to their inherent properties, including high strength and stiffness, dimensional stability, low coefficient of thermal expansion, biological compatibility, and fatigue resistance. In this chapter, we have classified the carbon fibers based on their performance, precursors, and commercial availability. Their unique characteristics have also been described.

1.4.1 Performance

Carbon fibers have been classified on the basis of the fiber structure and degree of crystallite orientation: ultrahigh-modulus (UHM), high-modulus (HM), intermediate-modulus (IM), high-tensile-strength (HT), and isotropic carbon fibers. Broadly speaking, these types have been categorized into three or four groups as listed in Table 1.1.

The UHM and HM carbon fibers are highly graphitized and characterized by a high modulus. The UHM carbon fibers are characterized with a modulus greater than 500 GPa, while the HM carbon fibers are characterized with a modulus greater than 300 GPa and a strength-to-modulus ratio of less than 1 %.

The IM and HT carbon fibers have high strength and low modulus owing to the heat treatment at lower temperatures. The IM carbon fibers have a modulus of up to 300 GPa and a strength-to-modulus ratio of $>1 \times 10^{-2}$. The HT carbon fibers are

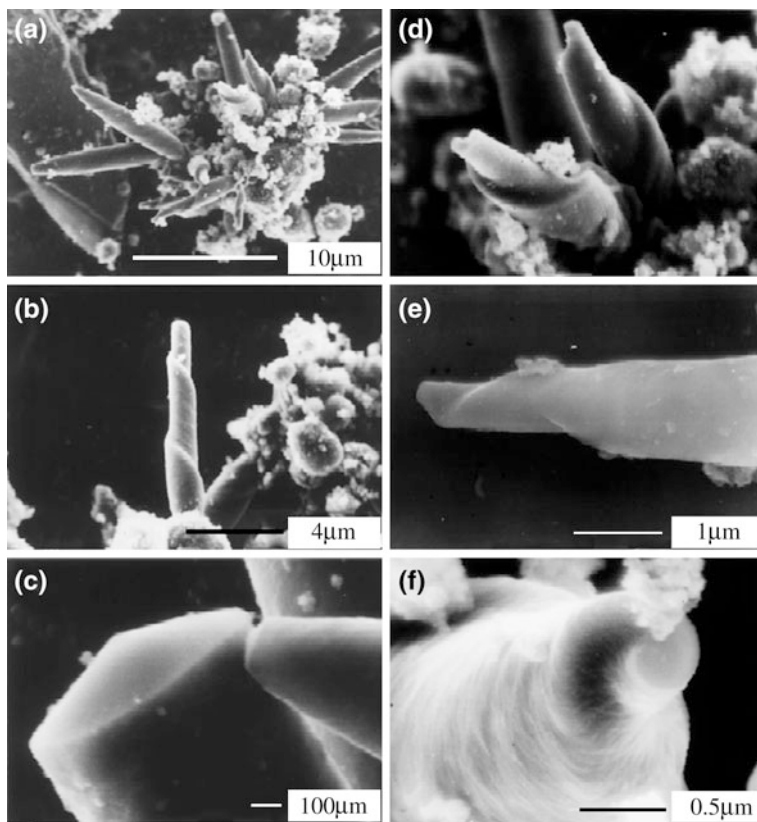
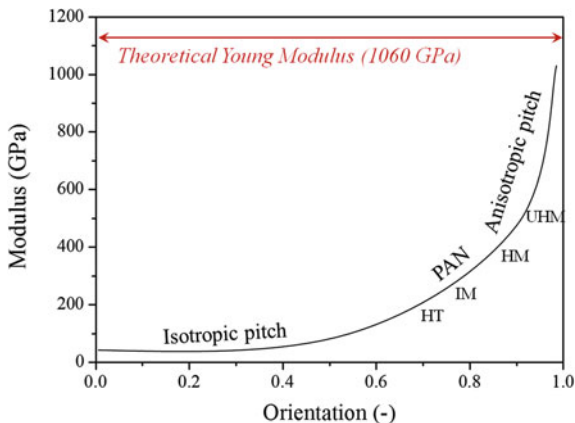


Fig. 1.9 Field emission scanning electron micrographs of whiskers growing at 2,100 °C and 100 Pa: **a** aggregation of several whiskers with different morphologies on ground graphite particle; **b** a whisker with long spiral; **c** fracture surface of a whisker with *conical shape* proves that the whisker is composed of conical carbon layers; **d** a couple of whiskers with different spirals; **e** a whisker with two different spirals; and **f** *top view* of tip of a whisker with spiral [35]

Table 1.1 Classification of carbon fibers

Carbon fiber type	Heat treatment temperature (°C)	Crystallite orientation	Long-distance order	
Type I high modulus	>2,000	Mainly parallel to the fiber axis	High	UHM
				HM
Type II high strength	≈1,500	Mainly parallel to the fiber axis	Low	IM
				HT
Type III isotropic	<1,000	Random	Very low	Isotropic

Fig. 1.10 Correlation of orientation and Young's modulus for carbon fibers made from different precursor systems: PAN, isotropic pitch, and anisotropic pitch (mesophase pitch) [37]



characterized with strength greater than 3 GPa and a strength-to-modulus ratio lying between 1.5 and 2×10^{-2} .

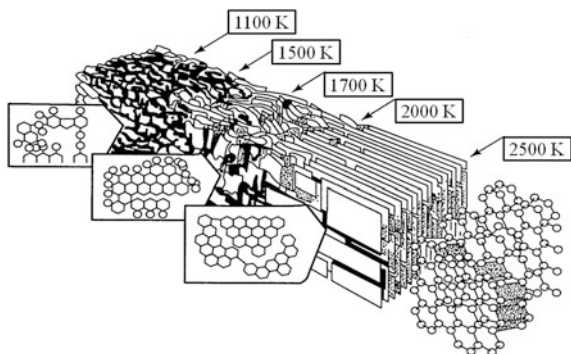
Finally, the isotropic carbon fibers show a random orientation of the crystallites and possess a modulus as low as 100 GPa combined with low strength. Their main advantage is low cost (Fig. 1.10).

1.4.2 Precursor

Carbon fibers are manufactured from synthetic fibers (precursor fibers) through heating and stretching treatments. The processing of carbon fibers from different precursors requires different conditions to obtain the satisfactory quality end products. The essential features are similar. The processing paths for various precursors are similar at the macrolevel. In addition, the precursor materials of the carbon fibers are important because the combination of various properties and behaviors (mechanical, physical, and chemical) on the carbon fibers depends on strongly on the starting precursor materials [38–42].

Generally, the carbon fibers are synthesized through a controlled pyrolysis of the stabilized precursor fibers (Fig. 1.11) [43, 51]. The precursor fibers were first stabilized and stretched over the temperature range 200 – 400 °C in air using an oxidation process (thermoset treatment), which strongly depended on the natural chemistry of the precursor. Then, in the carbonization process, the stabilized fibers were subjected to high temperatures over the range 800 – $1,600$ °C in an oxygen-free environment to remove noncarbon impurities, including hydrogen, oxygen, nitrogen, and other noncarbon elements. Further, the carbonized fibers were graphitized using a graphitization process involving higher temperatures of up to $3,000$ °C, which stretched the fibers resulting in 50 – 100 % elongation. The stretching of fibers ensured a preferred crystalline orientation, which resulted in the desired modulus being higher than those of carbonized fibers. The properties of the resultant carbon

Fig. 1.11 Structural model for carbon fibers during graphitization process [51]



fibers were relevant to their crystallinity, crystalline distribution, carbon content, molecular orientation, and the proportion of defects. Finally, the surface treatment processes and epoxy sizing of carbon fibers, i.e., posttreatment processes, were performed to enhance their adhesion to the composite matrices [44–50].

It is known that the polyacrylonitrile (PAN), pitch, and rayon are the three most common precursors for the carbon fibers. A simplified schematic of the process for the preparation of precursor and typical carbon fibers is presented in Fig. 1.12. The process for the manufacturing of PAN-based carbon fibers and pitch-based carbon fibers are shown in Figs. 1.13 and 1.14, respectively.

Figure 1.15 explains in detail the basic chemistry and physics of different processes for fabrication. In case of the PAN fibers, the stretching of the coiled macromolecule in the direction of the polymer chain was parallel to the fiber axis and the subsequent transformation of the linear molecule into a ladder polymer was observed. The PAN-based precursor fibers are usually fabricated using the conventional spinning technique such as wet spinning. They must be converted to a form which is flameproof and stable at the high temperatures involved in carbonization. Consequently, before carbonization, they are stabilized in the case of the PAN precursor in an oxidizing atmosphere.

In the case of the pitch fibers, the preferred orientation was realized by the spinning process of the liquid crystals in the pitch (melt spinning and melt blowing methods) [52–59], which consisted of polyaromatic molecules, in a direction

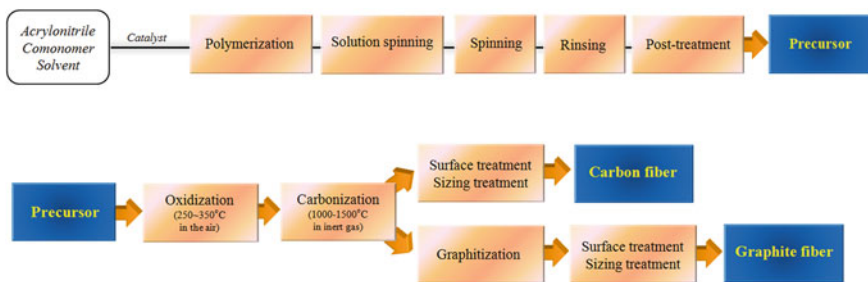


Fig. 1.12 Typical schematic of the process for preparation of precursor and typical carbon fibers

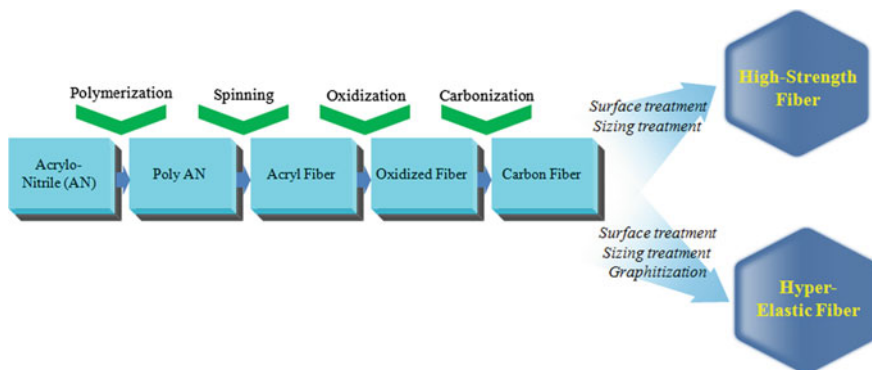


Fig. 1.13 Manufacturing process for PAN-based carbon fibers

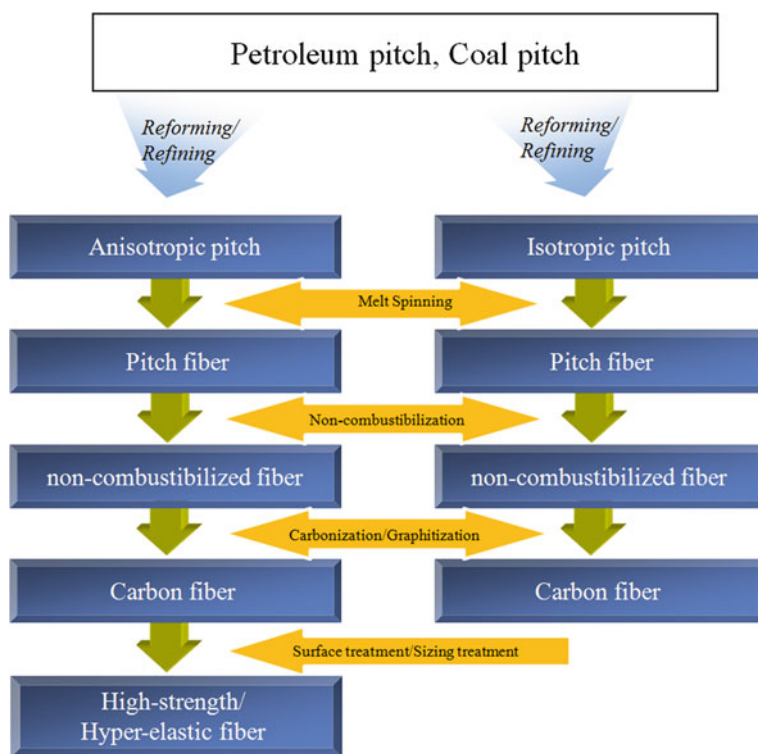


Fig. 1.14 Manufacturing process for pitch-based carbon fibers

parallel to that of the fibers [55]. The step in the pitch process, involving the introduction of the structurally preferable orientation of the planar molecules, has to be combined with chemical treatment to conserve the resulting carbonaceous defect

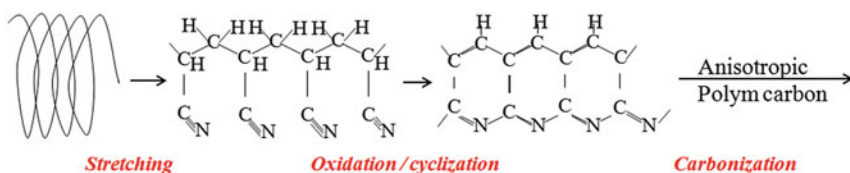
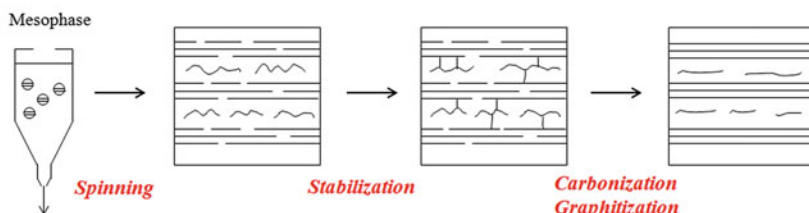
ORIENTATION DURING STRETCHING (PAN)**ORIENTATION DURING SPINNING (PITCH)**

Fig. 1.15 Two types of fabrication processes

structure during all the subsequent heat treatment processes. Since the last 100 years, it is well known in the graphite industry what type of thermally stable defect structures form by the carbonization of thermosetting polymers. On the other hand, nonstable defect structures, i.e., well-graphitizing cokes, could be achieved by the carbonization of carbon–hydrogen compounds in a fluid state. From these general rules, it is believed that the PAN-based precursor fibers prepared by the cyclization of PAN polymers must yield either nongraphitizing carbon or carbon fibers with a thermally stable, defective structure. In contrast, the anisotropic pitch-based carbon fibers possess the ideal preconditions for good graphitization. This capability of the anisotropic pitch must be destroyed before carbonization by forced oxidation and cross-linking reactions.

Meanwhile, the pitch precursors are divided into the isotropic and anisotropic pitches (mesophase pitch) based on their optical characteristics. On the basis of their mechanical properties, pitch-based carbon fibers can be further classified into high-performance (HP) carbon fibers (HP-carbon fibers) and general-purpose carbon fibers (GP-carbon fibers). The isotropic pitch forms an isotropic carbon fiber, which belongs to the category of GP-carbon fibers, whereas the anisotropic pitch forms HP-carbon fibers, wherein the carbon layers are preferentially parallel to the fiber axis.

The pitch is usually derived as a by-product from either coal- or petroleum-based chemistry. The pitch from petroleum is preferred because the coal pitch is difficult to clean owing to natural inclusions as defect-sensitive particles. In contrast to the PAN-based precursors, the pitch is a low molecular weight material.

In addition, the synthetic pitch could be produced from the synthetic polymers such as polyvinyl chloride (PVC) and naphthalene [56]. Ohtani [57] reported the

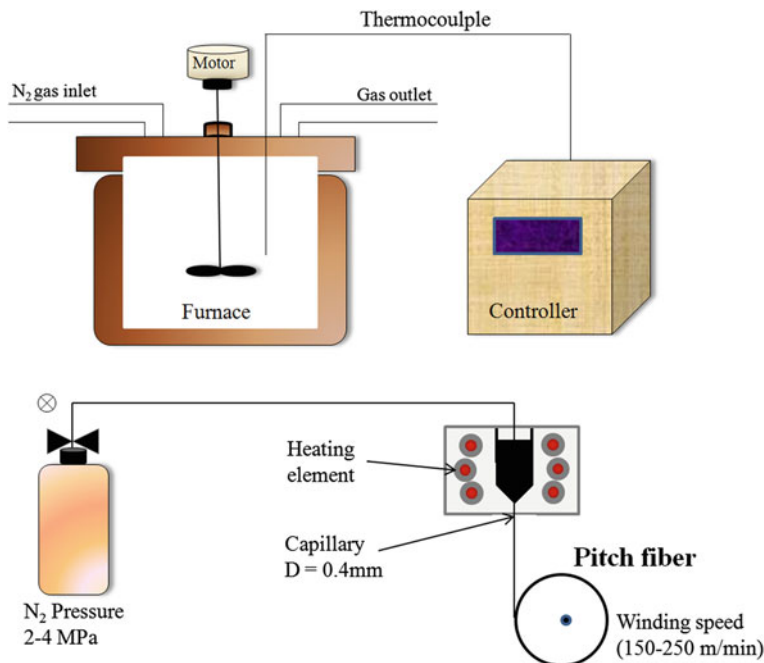


Fig. 1.16 Schematic of reactor and melt spinning apparatus [59]

molten pyrolysis product of PVC for manufacturing carbon fibers. This method suggested the possibility of utilizing tar pitches from oil refinery and coal pyrolysis processes as new precursors for carbon fibers. Today, pitch-based carbon fibers have been introduced in the market [58].

Wazir and Kakakhel reported that when a petroleum pitch was heated at 420 °C for 7 h in a nitrogen atmosphere, a carbon fiber precursor is formed with a softening point of 295 °C. The precursor was successfully melt-spun into fibers through a circular nozzle of a monofilament spinning apparatus. Wazir and Kakakhel [59] focused on optimizing the operating conditions for melt spinning of the precursor pitch (Fig. 1.16).

Rayon-based carbon fibers are obtained from the rayon precursor fibers using chemical pretreatments and carbonization. These are isotropic carbon fibers and can be transformed into anisotropic carbon fibers with high strength and stiffness by stretching at temperatures above 2,500 °C. However, as shown in Fig. 1.17, all glycosidic bonds generate volatile carbon dioxide during pyrolysis. It is difficult to avoid the fracture of the bimolecular unit of the polymer in the volatile ether glucosan. Mass loss from the polymer structure at different stages of pyrolysis causes an enormous amount of shrinkage, resulting in a low carbon yield of <30 %. Consequently, an extremely porous carbon residue with low density is formed.

Figure 1.18 shows the carbon yields of aromatic polymers such as poly(p-phenyleneacetylene) and others, compared to those of rayon, PAN, and pitch [60, 61].

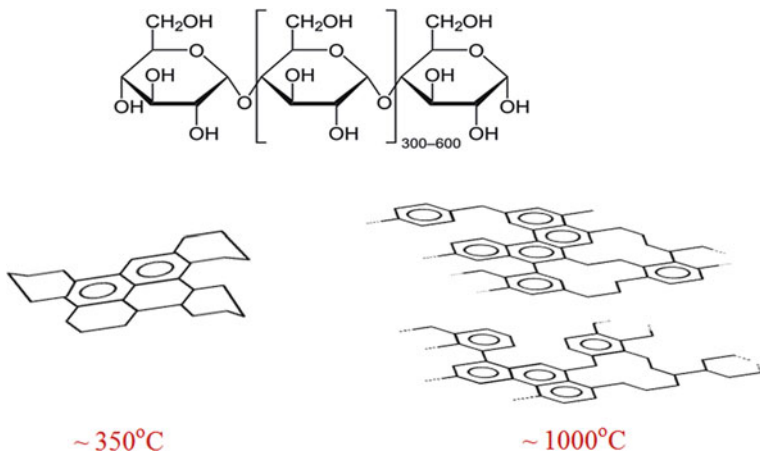


Fig. 1.17 Schematic of thermal degradation of cellulose to carbon

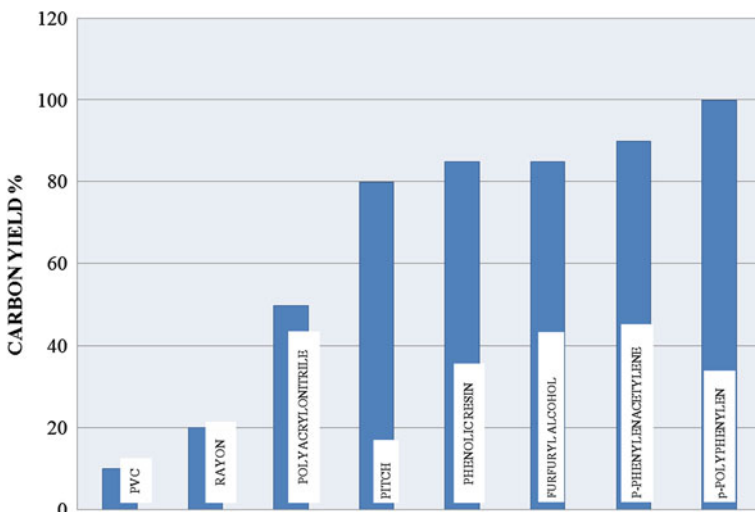


Fig. 1.18 Comparison of carbon yield of polymers after pyrolysis

It is well known that there are primarily three types of precursor materials of commercial significance, as previously mentioned, PAN, pitch, and rayon. Although the worldwide production of carbon fibers has increased rapidly, the prohibitive cost of carbon fiber production and high demand limit the widespread use of carbon fibers. The overall challenge is the combination of precursor cost, yield, processing cost, and similar factors.

In addition, carbon fibers have been previously manufactured from lignin. Lignin-based carbon fibers such as Kayacarbon were first developed and made

commercially available by Nippon Kayaku Co. on a pilot scale. The process involved carbonization of dry-spun fibers from lignin dissolved in an alkali solution containing poly(vinyl alcohol) as a plasticizer [62–64].

Lignin, second only to cellulose in natural abundance, is readily available, relatively inexpensive and structurally appealing as a precursor for carbon fibers. It is a high molecular weight polyaromatic macromolecule with a reported total worldwide production of approximately 26 million ton/year [65].

However, lignin-based carbon fibers have a low tensile strength of approximately 0.3 GPa, in comparison with typical commercial PAN-based carbon fibers (above 3.5 GPa). Thus, a few researchers have reported the lignin-based carbon fibers with mechanical properties, which are suitable for either general purpose (GP) or above grades, through the various pretreatment processes of lignin [66–68]. Kadla et al. [69] have reported the lignin-based carbon fibers modified by the Kraft process (a process for converting wood into wood pulp comprising almost pure cellulose fibers) and blends, thereby reaching a tensile strength of approximately 0.5 GPa and a modulus of up to 60 GPa. Kubo et al. [70] have investigated lignin-based carbon fibers by blending them with PET, which resulted in a tensile strength of 0.7 GPa and a modulus of 94 GPa. A more recent investigation by the Oak Ridge National Laboratory (ORNL) on lignin-based carbon fibers revealed a tensile strength of approximately 0.51 GPa and a modulus of 28.6 GPa (Fig. 1.19) [71].

Fig. 1.19 Fiber spools produced from organic-purified hardwood lignin utilizing pilot scale unit with 12-hole spinneret [71]



Despite the weak mechanical properties, the development of processes utilizing lignin, as a low-cost and renewable resource precursor material for low-cost carbon fiber production, has been relentlessly pursued. A few studies reported the possibility of producing carbon fibers from lignin. Also, the modification of lignin for producing HP-carbon fibers has been studied using purification, chemical modification, and plasticization [72–76].

Short carbon fibers are being rapidly developed through preparation in the vapor of hydrocarbon atmosphere with low molecular weight compounds, including acetylene and ethylene. This process involves catalytic growth using solid catalyst particles (Fe, Co, and other transition metals) to form carbon filaments, which could be as small as 0.1 μm in diameter. They consist of graphitizable carbon and could be transformed into graphite fibers by heat treatments above 2,500 $^{\circ}\text{C}$. Then, subsequent chemical vapor deposition from the carbonaceous gas in the same chamber caused the filaments to grow in diameter, resulting in vapor-grown carbon fibers (VGCFs) or gas-phase-grown carbon fibers [77–80].

Unlike the complex PAN-based processes, the manufacturing process for “vapor-grown” production technology is simpler, faster, and cheaper. As indicated in Fig. 1.20, VGCFs are produced in the vapor phase by decomposing methane, ethane, or coal gas in the presence of a metal catalyst, hydrogen sulfide, and ammonia. The catalyzed gas decomposes into carbon and hydrogen and gets conveyed to a reactor furnace. Carbon remains in the reactor for only a few milliseconds, growing into a fiber of 60–200 nm in diameter and approximately 100 μm in length. The fiber is

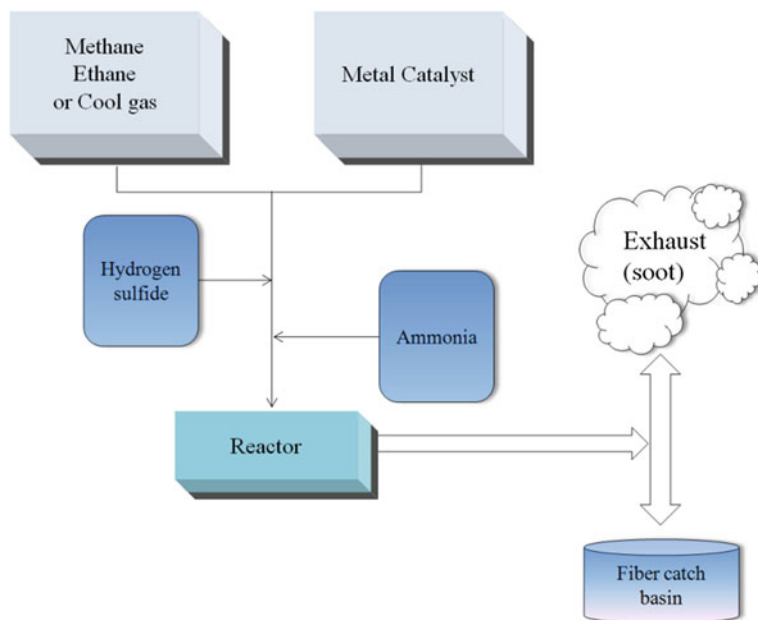


Fig. 1.20 Vapor-grown carbon fiber manufacturing process

debulked for either sale or additional processing (such as heat treatment). In particular, the process of preparing VGCFs overcame many costly production steps and processing compared to those of the PAN-based process; it also provided an innovative approach for fabricating HP fibers at lower costs.

1.4.3 Commercial Availability

Carbon fibers could alternatively be classified on the basis of their commercial availability, namely GP-, HP-, and activated carbon fibers (ACF).

The GP-carbon fibers have low tensile strength, low tensile modulus, and low cost because of their amorphous and isotropic structures. The greatest advantage of these carbon fibers is their low cost. The short GP-pitch-based carbon fibers are used in the reinforcement of concrete because it is easy to use in large quantities. The GP-carbon fibers are also used for thermal insulation, sealing materials, electrically conducting materials, antistatic materials, heating elements, filters, fraction materials, sorbents, and catalysts [81].

The HP-carbon fibers are characterized by high strength and modulus in comparison with the GP-carbon fibers. Among the HP-carbon fibers, a higher modulus is associated with a higher proportion of graphite and more anisotropy. The HP-carbon fibers are widely used in polymer–matrix composites for aircraft, which are lightweight for the purpose of saving fuel. Nearly 90 % of the structure of the aircraft, Voyager, is made of such composites. In 1986, the Voyager successfully performed a nonstop, unfueled, round-the-world flight. The use of such composites in passenger aircraft is rapidly rising. The HP-carbon fibers are also used in carbon–matrix composites for high-temperature aerospace applications such as the Space Shuttle, as the carbon matrix is more temperature resistant compared to a polymer matrix. These fibers are now used in metal matrices such as aluminum for aerospace applications as aluminum is more temperature resistant compared to polymers.

Finally, ACFs have a large specific surface area and micropore volume for the adsorption of either gas or liquid. Compared to the conventional granular or powder activated carbons, ACFs have been widely used in the separation, purification, and catalytic processes owing to their extended specific surface area, high adsorption capacity, highly porous structure, and special surface reactivity. ACFs have been used not only as reducing agents by themselves but also as catalyst supports for removing pollutants such as NO_x , SO_x , NH_3 , and even HCl [82–106]. Also, the microstructure of ACFs is created during the activation and is affected by many factors such as the degree of activation and carbonization conditions [107]. The adsorption/desorption rate of carbonaceous adsorbents is greatly dependent on not only microporous structures but also surface properties [108–110].

Most recently, ACFs have been drawing attention as adsorbents for hydrogen storage and capture of CO_2 from a thermal power plant. ACFs offer several advantages in terms of cost with rapid adsorption kinetics, availability, large surface area, easy-to-design pore structure, easy surface functionalization, hydrophobicity,

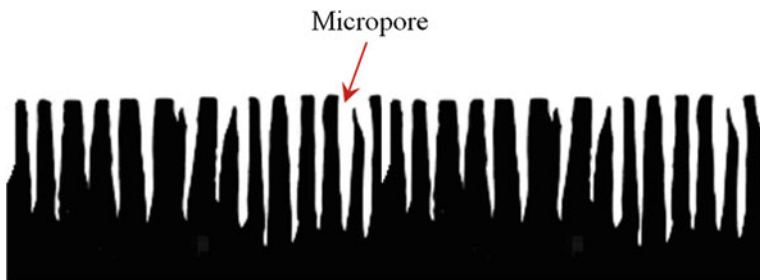


Fig. 1.21 Pore shape and structure of activated carbon fibers

reversibility, and low energy requirements for regeneration. With regard to gas adsorption, ACFs are also considered promising materials because of their nano-structure, abundant micrometer porosity, and properties such as high specific surface area and narrow pore size distribution. The fibrous shape of ACFs has the advantage of easy handling compared to granular and powdered adsorbents [111–115].

In particular, the amount of CO₂ adsorbed by the ACF samples (modified by thermally chemical activation) was substantially higher than that obtained for most other well-known adsorbent materials designed for CO₂ capture, including MOF-5, zeolite (Fig. 1.21), and activated carbons [116]. This is because of their well-developed pore structures and inherent CO₂ affinity of ACF surfaces for high-performance CO₂ capture (Fig. 1.22).

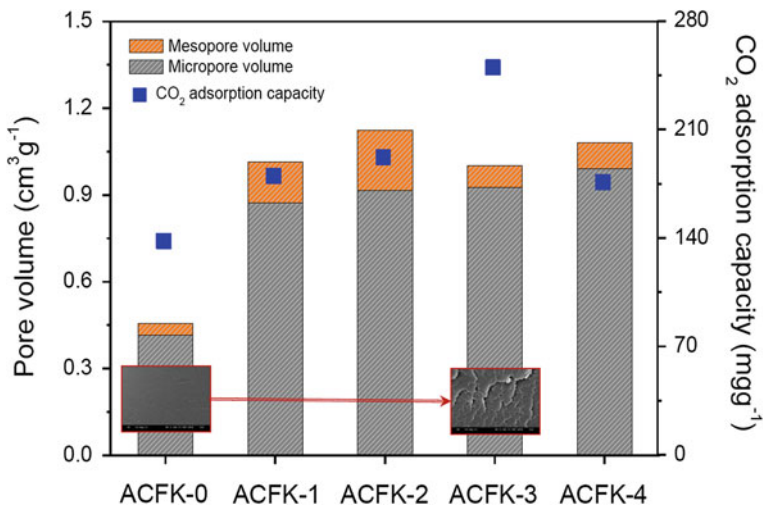


Fig. 1.22 Relationship between micro/mesopore volume ratios and CO₂ adsorption capacity of ACFK samples at various KOH ratios (*inset SEM images before and after KOH heat treatment*)

1.5 Structure of Carbon Fibers

Carbon fibers generally have excellent tensile properties, low densities, and high thermal and chemical stabilities in the absence of oxidizing agents, good thermal and electrical conductivities, and excellent creep resistance. They have been extensively used in composites in the form of woven textiles, prepregs, continuous fibers/rovings, and chopped fibers. The composite parts could be produced through filament winding, tape winding, pultrusion, compression molding, vacuum bagging, liquid molding, and injection molding.

Several techniques, including wide- and small-angle X-ray diffraction, electron diffraction, transmission, scanning and surface replica electron microscopy, and optical microscopy, have been investigated for the structure of carbon fibers [117–121]. From these techniques, valuable information about the various micro- and macroaspects of the fiber structure has been provided continually hitherto such as qualitative and quantitative information about several structural parameters, including crystallite size and orientation, stack height and width, shape and size of pores, and presence of three-dimensional order.

Here, we will briefly summarize the unique structures of carbon fibers as discovered using X-ray diffraction and electron microscopy, which are the simplest and most effective techniques for the elucidation and foundational understanding of the basic science of structure in carbon fibers.

Carbon fibers could be either short or continuous. In addition, the structure of carbon fibers could be crystalline, amorphous, or partly crystalline. The atomic structure of a carbon fiber is similar to that of graphite wherein the c -direction distance between the layer planes is 3.35 Å (d-spacing, $d_{(002)}$) and consists of carbon atom layers arranged in a regular hexagonal pattern (as previously shown in Fig. 1.1). It has a high modulus, 0.18–0.35 GPa; however, in humid atmosphere, its shear strength is weak along the a -axis.

In graphitic crystalline regions (microdomains), the crystal structure of carbon fibers consists of sp^2 hybridized carbon atoms arranged two-dimensionally in a honeycomb structure in the x - y plane with van der Waals forces, which are stacked parallel to one another in a regular fashion. In the graphite layer, the carbon atoms are bonded covalently and through metallic bonds owing to the overlap of the sp^2 hybridized orbital and delocalization of the p_z orbitals (the π electrons), respectively. The good electrical and thermal conductivity of graphite are attributable to the delocalization in the x - y plane.

However, the basic structural unit of most of the carbon fibers consists of a stack of turbostratic layers. In a turbostratic structure, the distance between the parallel graphene sheets is greater than that in graphite (Fig. 1.23). The basic structural unit could either irregularly or haphazardly split, tilt, twist, fold, and join other basic structural units to form microdomains. As shown in Fig. 1.24, these microdomains could also split, tilt, twist, fold, and join each other in carbon fibers [121]. Thus, the structure of carbon fibers is not homogeneous. It has been

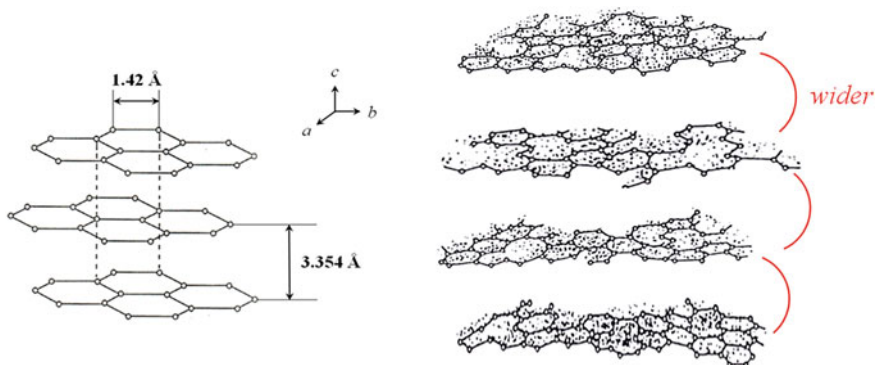
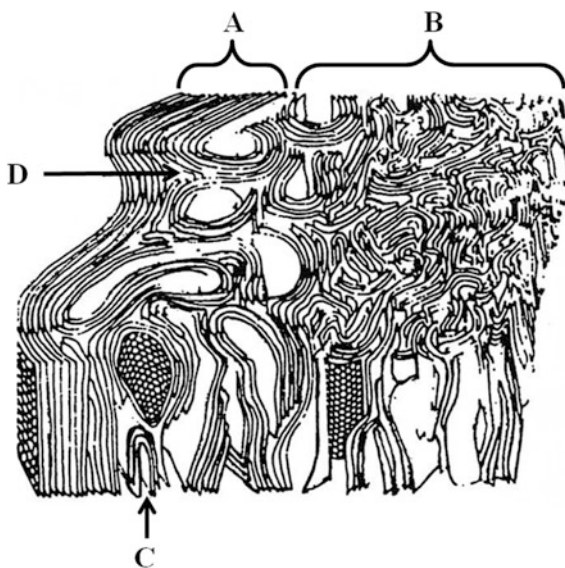


Fig. 1.23 Crystal structure of a graphite crystal (*left*) and structure of turbostratic carbon (*right*)

Fig. 1.24 Combination of basic structural units into microdomains within a carbon fiber: *A* skin region; *B* core region; *C* a hairpin defect; and *D* a wedge disclination [119]



reported that the irregular stacking and presence of sp^3 bonding could increase the d-spacing to 3.44 Å [122, 123].

Johnson and Watt [124] have investigated the crystallite structure of PAN-based carbon fibers treated at 2,500 °C and found that the turbostratic crystallites had L_c (crystallite height) of at least 12 layer planes and L_a (crystallite width) of 6–12 nm. Both L_c and L_a tended to increase with the heat treatment temperature.

The basic structural unit and some of the microdomains were initially established by the fiber formation process, including the precursors and processing conditions.

Generally, it is known that a well-stacked graphitic crystalline structure could only be observed in the mesophase pitch and vapor-grown carbon fibers, while the turbostratic structure could be observed in carbon fibers with other precursors such

as PAN. In the graphitization of stabilized PAN-based fibers, the crystalline domain is developed by either amalgamating with adjacent crystallites or incorporating the surrounding disorganized carbons. Furthermore, the layer planes within the crystalline domain relocated through rotating and shifting. However, these arrangements had appeared locally and the graphite fibers still possessed significant turbostratic domains with the existence of extensive rotational disordering of layer planes.

Bourrat et al. [125] reported that noncarbonized mesophase pitch-based fibers exhibited three levels of structural organization. The same three levels of organization, with slight modification, could be applied to all types of carbon fibers. These are as follows:

1. At the molecular range level, molecules are stacked together creating small coherent domains, as in the starting mesophase pitch, known as “basic structural units.”
2. At the next level of organization, i.e., from one to a few hundred nm, a microtexture is observed. It is defined by microdomains which consist of assemblies of molecules with a long-range orientation order. These microdomains are elongated along the fiber-axis direction, up to several μm , and limited laterally by pores and wedge disclinations. The descriptive “micro” is used here to specify this level of organization. The characteristics of the basic structural unit and microtexture are determined using a combination of wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), selected area diffraction (SAD) by transmission electron microscopy (TEM), and use of bright- and dark-field imaging in the TEM.
3. The last level of organization defines the fibers’ texture. It reflects the changing statistical orientation of the molecules at a very long range. The texture is readily observed in the SEM and could be deduced through the optical microscope studies with the aid of reflected polarized light (detailed information and optical images are shown in [125]).

Figure 1.25 shows the basic structural unit at the several stages during the conversion of a fiber from the stabilized material to graphite. At low temperatures, after stabilization, the oriented basic structural units were isolated and the hetero atoms were eliminated at the higher temperatures. Then, some stacks were formed by assembling the oriented basic structural units, which led to the creation of pores and increase the densification. At higher temperatures, some microdomains were formed as the dense and orderly structures. At further higher temperatures, disordered layers of turbostratic carbon appeared. Finally, at extreme temperatures, planar layers of graphite resulted. The change in the perfection and ordering of carbon in fibers could be readily observed using high-resolution electron microscopes.

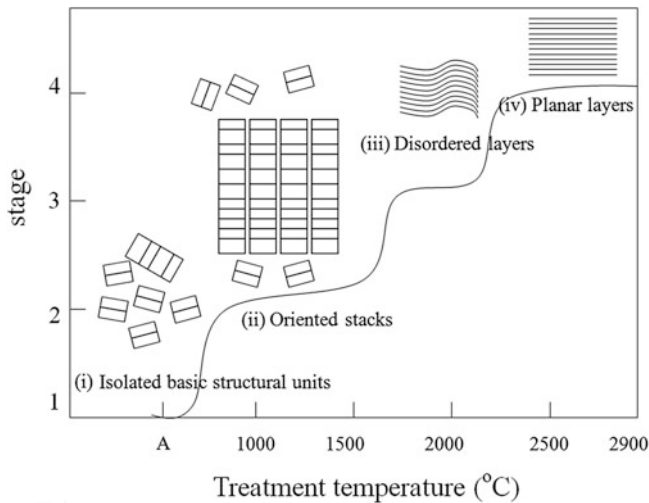


Fig. 1.25 Various stages of graphitization and sketches of structures (At point A: nonheat-treated carbonaceous materials) [125]

1.6 State of Carbon Fiber Industry

1.6.1 Technology Development Trends

Carbon fibers have remarkable properties such as tensile strength, stiffness, low density, electrical conductivity, and chemical inertness. Carbon fibers have been used to manufacture sports cars as well as sports equipment such as fishing rods, golf shafts, and tennis racquets. Currently, a great deal of attention is being paid to reduce the weight of passenger vehicles to increase vehicle fuel economy and lower the greenhouse gas emissions. Thus, carbon fibers are now used in aircraft and industrial applications such as pressure vessels, windmills, civil engineering/construction-related uses, and cars and yachts.

However, owing to the tricky and multistage manufacturing processes of carbon fibers, only eight companies, including Toray, Toho Tenax, Mitsubishi Chemical, Hexcel, and Zoltek, have succeeded in the mass production of carbon fibers. In each country, the export of carbon fibers is strictly prohibited because carbon fibers are widely used in the state-of-the-art weapons. In addition, historically, the carbon fiber industry has been cyclical with a period of limited supply resulting in high prices to periods of oversupply resulting in falling prices.

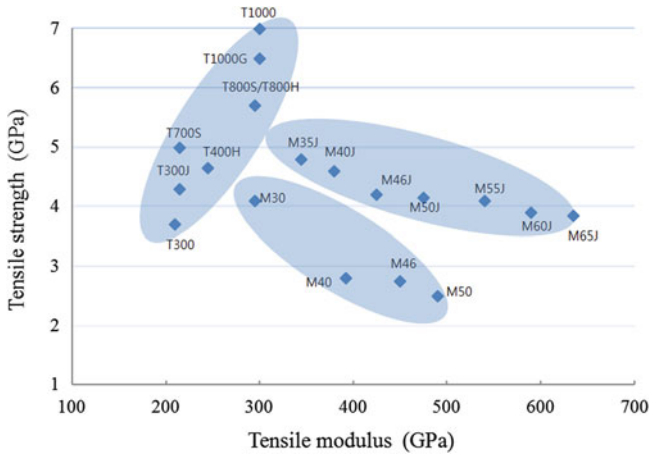


Fig. 1.26 Classification of high-performance carbon fibers (Toray) [127]

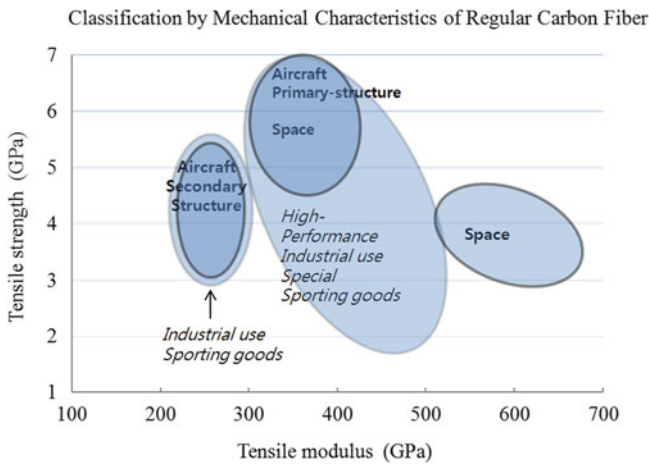


Fig. 1.27 Applications based on mechanical characteristics of regular carbon fibers (Torayca) [127]

Toray leads in the development of high-performance carbon fibers. Figure 1.26 shows the classification of high-performance carbon fibers made by Toray. In particular, T (Torayca)-1,000 contains high-performance carbon fibers with a tensile strength of 7 GPa and a tensile modulus 300 GPa, which enabled the diversification of the application fields. Figure 1.27 presents the application based on the mechanical characteristics of regular carbon fibers [127].

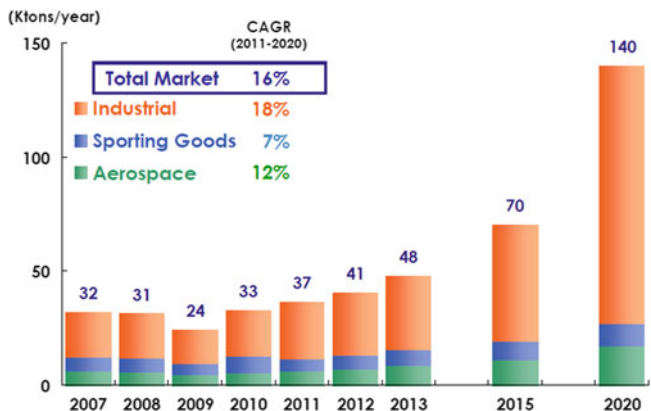


Fig. 1.28 Carbon fibers market trends and compound annual growth rate (CAGR) of carbon fiber applications (Toray) [127]

1.6.2 Utility Development Trends

Figure 1.28 shows the trends and compound annual growth rates (CAGR) of carbon fiber applications until 2020 [127]. After the storm of the financial crisis in 2009, the market for carbon fibers gradually increased. The demand for carbon fibers is classified into industrial, sporting goods, and aerospace applications. The sporting goods is one of the oldest applications for carbon fibers, but it is experiencing only modest growth, as there are no new significant applications to be expected.

The industrial sector of the market breadth and CAGR has led to the expanded market for carbon fibers. The industrial sector is also growing in importance with a wide range of applications. The industrial sector overall, excluding aerospace and sporting goods, is forecast to represent more than 75 % of the total usage of carbon fibers by 2020 (see below).

- Energy: blades for wind power, pressure vessels, electrode gas diffusion layers for fuel cells, offshore oil industry, high-risers;
- Transportation: vehicle parts (for weight reduction, safety, and environment), marine parts (decks, hulls, and masts);
- Civil engineering (antivibration plate, bridges, and lightweight buildings);
- Industrial equipment: rollers for printing machines, PC frames, machine components, medical components.

It is noteworthy that the demand for carbon fibers will increase with the increasing quality of the entire life cycle and the importance of the environmental issues.

In the meantime, the CAGR of the aerospace sector is somewhat sluggish. In the next few years, it is expected to increase substantially owing to the demand of large aerospace companies (such as Boeing and Airbus) for the development of carbon fiber composites, which could result in the weight reduction and fuel savings.

1.6.3 Market Trends

Since 1971, Toray Co. [127] has been manufacturing PAN-based carbon fibers using a proprietary technology and became the top carbon fiber manufacturer in the world, capturing 34 % (regular tow) of the global market share with a production capacity of 7,600 ton/year. Toray has shifted its focus from the aviation, space, sports, and industrial sectors and directed attention toward the carbon fiber composites for the Boeing Aircraft. In addition, they have developed the carbon fiber manufacturing techniques such as precursor emulsion, stretching, mixed spinning, carbonization/graphitization techniques for carbon fibers, and molding of carbon fiber composites to obtain the high-performance carbon fibers. The steady development of a variety of purposes and usages for the carbon fibers has been observed. Toho Tenax Co. [128], since 1975, has manufactured high-performance PAN-based carbon fibers and flame-retardant fibers. It ranked second in the world with a production capacity of 5,600 ton/year. The company has also gained recognition in the aircraft industry. They supplied the entire structural components required for manufacturing vertical tail wings and flooring of Airbus A380, which occupies part of the 70 % of the aircraft industry. Toho Tenax Co. has also developed industrial components such as spring, rotor, and brake, and reinforced technology for concrete structure. Since 1976, Mitsubishi Chemical Co. [129] has produced prepregs using the high-performance carbon fibers obtained from Courtaulds Co. (England). Later, carbon fibers were produced through a technical partnership with HITCO Co. (USA) since 1983. With a production capacity of approximately 3,400 ton/year, Mitsubishi was ranked third in the world. Then, Hexcel Co. [130], Cytec Co. [131], and Formosa Co. [132] accelerated the manufacture and development of carbon fibers. Table 1.2 lists the PAN-based carbon fiber manufacturers and their markets in the world.

Table 1.3 lists the pitch-based carbon fiber manufacturers and their respective market shares in the world. As listed in Table 1.3, the pitch-based carbon fibers have a relatively smaller market size compared to the PAN-based carbon fibers. While the universal type of pitch-based carbon fibers was used as fillers and insulating materials, the high-performance pitch-based carbon fibers were competing with the PAN-based carbon fibers in the field of advanced composites materials, which resulted in the creation of a new market owing to their unique characteristics. In particular, it is expected that the mesophase pitch-based carbon fiber market will grow significantly in the aerospace sector for applications in extreme environments such as the structure of the antenna and exterior materials of electronic devices.

Table 1.2 PAN-based carbon fiber manufacturers and their respective global market shares [Unit: ton]

Division	2007	2008	2009	2010	2011	2012	2013*	Product name	Main fields
Toray	Zoltek (USA)	450	600	600	600	600	10,500	Panex	C/C composites (aircraft)
	Toray (Japan)	1350	1390	1390	1390	1390	7,300	Torayca	aircraft (Boeing)
	CFA (USA)	100	100	100	100	100	5,400	-	golf shafts
	Soficar (Toray Europe)	-	-	-	-	-	5,200	-	-
	Toray Advanced Materials (S. Korea)	-	-	-	-	-	2,200	-	-
	Toho Tenax (USA)	780	1050	1050	1050	1050	6,400	Besflight	aircraft (Airbus)
Mitsubishi Rayon	TTE (Germany)	-	-	-	-	-	5,100	-	-
	TTA (USA)	-	-	-	-	-	2,400	-	-
Formosa (Taiwan)	Mitsubishi Rayon (Japan)	740	740	740	740	740	8,100	Pyrofil	sporting goods
	Grafil (USA)	-	-	-	-	-	2,000	-	-
Hexcel (USA)	Formosa (Taiwan)	300	300	300	300	300	7,450	-	sporting goods
	Hexcel (USA)	380	380	380	380	380	5,700	-	aircraft
Aksa (Turkey)	SGL (Germany)	200	250	250	250	250	6,000	Panox	brake (aircraft)
	Aksa (Turkey)	-	-	-	-	-	3,300	-	-
Taekwang (S. Korea)	Cytec (USA)	200	200	200	200	200	2,400	Thornel	advanced composites
	Hyosung (S. Korea)	-	-	-	-	-	2,000	-	-
Quantity	Taekwang (S. Korea)	-	-	-	-	-	1,500	-	-
	Quantity	4500	5010	5010	5010	5010	82,950	-	-

A basis reference of Materials Technology Publications 2008 "The Carbon Fiber Industry"

* The manufacturing capacity of PAN-based carbon fibers in 2013 has been updated with reference to "Chemical Journal's Report" issued on July 2014.

Table 1.3 Pitch-based carbon fiber manufacturers and their global market shares [Unit: ton]

	2007	2008	2009	2010	2011	2012	2013	Product name	Main fields
Anisotropy	Mitsubishi Chemical (Japan)	75	100	125	125	125	125	Dialead	aircraft, aerospace, electric components, cement reinforcement
	Nippon Graphite (Japan)	12	12	18	18	40	40	Granoc	aircraft, aerospace, civil construction, sports
	Cytec (USA)	36	36	36	36	36	36	Pitch Thormel	high thermal conductivity/structure/friction
	Quantity	123	148	154	179	201	201	-	-
Isotropy	Petoca Materials (Japan)	120	120	120	120	120	120	Melblown	electrode, capacitors, heating
	Kureha Chemicals (Japan)	90	90	90	90	90	90	Kreca	curtain wall, insulation, electromagnetic shielding
	Donac	30	30	30	30	30	30	-	electromagnetic sealer
	Quantity	240	240	240	240	240	240	-	-
	Total amount	363	388	394	419	441	441	441	-

A basis reference of Materials Technology Publications 2008 "The Carbon Fiber Industry"

1.7 Summary

In this chapter, we have provided a brief overview of carbon fibers, showing superior performance and comprising expensive materials, in that the origin, history, manufacturing technology, performance, and world market trends.

Despite the high performance, the carbon fibers were only used for military purposes and aerospace/aviation owing to the higher price. Recently, carbon fibers have attracted attention for their potential use as structural materials in aerospace, sports, cars, and bridges. Also, carbon fibers have been considered as the next-generation materials in the aerospace/aviation industry, which has presented a huge opportunity to the entire supply chain of carbon fibers.

References

1. H.O. Pierson, *Handbook of Carbon, Graphite, Diamond and Fullerenes*. (Noyes Publications, Park Ridge 1993)
2. R.F. Furl, R.E. Smalley, *Sci. Am.* **265**, 54 (1991)
3. A.R.G. Brown, W. Watt, R.W. Powell, R.P. Tye, *J. Appl. Phys.* **7**, 73 (1956)
4. G.M. Jenkins, K. Kawamura, *Nature* **231**, 175 (1971)
5. S. Dimovski, Y. Gogotsi, Chapter 4. Graphite Whiskers, Cones, and Polyhedral Crystals, in *the Carbon Nanomaterials*, CRC Press (2006)
6. T.V. Hughes, C.R. Chambers, Manufacture of carbon filaments, US Patent 405, 480 (1889)
7. R.T.K. Baker, P.S. Harris, M. Dekker, *New York* **14**, 83 (1978)
8. G.G. Tibbetts, Vapor-Grown Carbon Fibers, in *Carbon Fibers Filaments and Composites*, ed. by J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Hüttinger (Kluwer, Dordrecht, 1990), pp. 73–94
9. P. Gadelle, The Growth of Vapour Deposited Carbon Fibres, in *Carbon Fibers Filaments and Composites*, ed. by J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Hüttinger (Kluwer, Dordrecht, 1990)
10. J.B. Donnet, R.C. Bansal, *Carbon Fibers* (Marcel Dekker Inc., New York, 1984)
11. J.B. Donnet, R.C. Bansal, *Carbon Blacks: Physics, Chemistry, and Elastomer Reinforcement* (Marcel Dekker Inc., New York, 1976)
12. H. Kroto, *Science* **242**, 1139 (1988)
13. S. Iijima, *Nature* **354**, 56 (1991)
14. A.K. Geim, K.S. Novoselov, *Nat. Mater.* **6**, 183 (2007)
15. T.A. Edison, U.S. Patent 223, 898 (1879)
16. X. Chao HU, H.H. Yang, *Compr. Comp Mater* **1**, 327 (2000)
17. N. Bhardwaj, S.C. Kundu, *Biotech. Adv.* **28**, 325 (2010)
18. A. Marcinčin, *Prog. Polym. Sci.* **27**, 853 (2002)
19. B.C. Elisa, M.M.V. Salim, P.B. Cristiano, *Carbon* **41**, 1707 (2003)
20. P.J.M Carrott, J.M.V Nabais, M.M.L Ribeiro Carrott, J.A. Pajares, *Carbon* **39**, 1543 (2001)
21. P.M. Sanjeev, C.H. Kim, S.Y. Kim, B.H. Kim, W.C. Kim, K.S. Yang, *Synth. Metals* **162**, 453 (2012)
22. W.M. Qiao, S.H. Yoon, Y. Korai, I. Mochida, S. Inoue, T. Sakurai, T. Shimohara, *Carbon* **42**, 1327 (2004)
23. E. Frank, F. Hermanutz, M.R. Buchmeiser, *Macromol. Mater. Eng.* **297**, 493 (2012)
24. J. Lin, K. Koda, T. Yamada, M. Enoki, Y. Uraki, *J. Wood Chem. Technol.* **34**, 111 (2014)
25. Y.Z. Wang, S.G. Wang, J.L. Liu, *Key Eng. Mater.* **575–576**, 151 (2014)

26. M. Zhang, A.A. Ogale, Carbon, (2013), Article in Press
27. A. Ju, H. Xu, M. Ge, J. Therm. Anal. Calorim. (2013), Article in press
28. M.R. Buchmeiser, J. Unold, K. Schneider, E.B. Anderson, F. Hermanutz, E. Frank, A. Müller, S. Zinn, J. Mater. Chem. **1**, 13154 (2013)
29. A. Ju, A. Liu, M. Luo, H. Xu, M. Ge, J. Polym. Res. **20**, 1 (2013)
30. Y.G. Ying, Y.P. Pan, R. Ren, J.M. Dang, C.L. Liu, Mater. Chem. Phys. **143**, 455 (2013)
31. Q. Hu, X. Wang, Z. Wang, Ceram. Int. **39**, 8487 (2013)
32. C. Dong, I.D. Davies, Mater. Des. **54**, 955 (2014)
33. E. Fitzer, D.D. Edie, D.J. Johnson, Carbon fibers-present state and future expectation; pitch and mesophase fibers; structure and properties of carbon fibers. in *Carbon Fibers Filaments and Composites*, 1st edn. ed. by J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Huttlinger (Springer, New York, 1989)
34. E. Fitzer, in *Carbon Fibers Filaments and Composites*, ed. by J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, and K.J. Huttlinger (Kluwer Academic, Dordrecht, 1990)
35. D. Jian, S. Wanci, Z. Baofa, L. Xuan, K. Feiyu, G. Jialin, L. Dongsheng, C. NanPing, Carbon **39**, 2325 (2001)
36. B.R. Growth, J. Appl. Phys. **31**, 283 (1960)
37. H. Herssler, Verstärkte Kunststoffe in der Luft- und Raumfahrttechnik. Kunststoffe und Elastomere in der Praxis (1986)
38. W. Bin, Z. Chun, X. Shijie, Z. Jing, X. Lianghua, J. Appl. Polym. Sci. **125**, 3545 (2012)
39. Y. Meijie, X. Yong, W. Chengguo, H. Xiuying, Z. Bo, Q. Kun, Y. Hua, J. Appl. Polym. Sci. **125**, 3159 (2012)
40. K. Kong, L.B. Deng, I.A. Kinloch, R.J. Young, S.J. Eichhorn, J. Mater. Sci. **47**, 5402 (2012)
41. S.Y. Gu, J. Ren, Q.L. Wu, Synth. Metals **155**, 157 (2005)
42. J.H. Kim, H.S. Ganapathy, S.S. Hong, Y.S. Gal, K.T. Lim, J. Supercrit. Fluids **47**, 103 (2008)
43. W. Meiyu, W. Qiaoying, L. Kaina, W. Yiqiong, L. Haiqing, Polym. Degrad. Stab. **97**, 1511 (2012)
44. A.R. Bunsell, *Fibre Reinforcements for Composites Materials* (Elsevier Science Publishers B.V., Amsterdam, The Netherlands, 1988)
45. Y. Ma, Z.H. Chen, Ceramic. Int. **38**, 4229 (2012)
46. F. Vautard, S. Ozcan, H. Meyer, Appl. Sci. Manufac. **43**, 1120 (2012)
47. P. Tsotra, K. Friedrich, Appl. Sci. Manufac. **34**, 75 (2003)
48. M.A. Montes-Morán, A. Martínez-Alonso, J.M.D Tascón, M.C. Paiva, C.A. Bernardo, Carbon **39**, 1057 (2001)
49. L.M. Manocha, Y. Eiichi, T. Yasuhiro, T. Shiushichi, Carbon **26**, 333 (1988)
50. S. Wei, G. Aijuan, L. Guozheng, Y. Li, Appl. Surf. Sci. **257**, 4069 (2011)
51. B.M. Parker, R.M. Waghorne, Composites **13**, 280 (1982)
52. D.D. Edie, Carbon **36**, 345 (1998).
53. N. Takami, A. Satoh, M. Hara, T. Ohsaki, J. Electrochem. Soc. **142**, 371 (1995)
54. N. Takami, A. Satoh, M. Hara, T. Ohsaki, J. Electrochem. Soc. **42**, 2654 (1995)
55. J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Huttlinger, in *Carbon Fibers Filaments and Composites* (Kluwer Academic Publishers, Berlin, 1990)
56. I. Mochida, K. Shimizu, Y. Korai, S. Fujiyama, H. Toshima, T. Hono, Carbon **30**, 55 (1992)
57. S. Ohtani, Carbon **3**, 31 (1965)
58. S. Sudo, K. Shimizu, J. Appl. Polymer Sci. **44**, 127 (2003)
59. A.H. Wazir, L. Kakakhel, New Carbon Mater. **24**, 83 (2009)
60. E. Fitzer, K. Müller, W. Schäfer, *Chemistry and Physics of Carbon* (Marcel Dekker, New York, 1971)
61. S. Otani, Y. Fukuoka, B. Igarashi, K. Sasaki, US Patent 3,461,082 (1969)
62. Y. Fukuoka, Jpn. Chem. Q **5**, 63 (1969)
63. Kayacarbon, Manufacturer's Brochure NKCL, 'Kayacarbon' Manufacturer's Brochure, Nippon Kayaku Co. Ltd., Japan

64. W.G. Glasser, S.S. Kelley, *Concise Encyclopedia of Polymer Science and Engineering* (Wiley, New York, 1990)
65. K. Sudo, K. Shimizu, N. Nakashima, A. Yokoyama, *J. Appl. Polym. Sci.* **48**, 1485 (1993)
66. S. Kubo, N. Ishikawa, Y. Uraki, Y. Sano, *Mokuzai Gakkaishi* **43**, 655 (1997)
67. Y. Uraki, S. Kubo, H. Kurakami, Y. Sano, *Holzforchung-Int. J. Bio. Chem. Phys. Tech. Wood* **51**, 188 (1997)
68. J.F. Kadla, S. Kubo, R.A. Venditti, R.D. Gilbert, A.L. Compere, W. Griffith, *Carbon* **40**, 2913 (2002)
69. S. Kubo, J.F. Kadla, *J. Polym. Environ.* **13**, 97 (2005)
70. D.A. Baker, N.C. Gallego, F.S. Baker, *J. Appl. Polym. Sci.* **124**, 227 (2012)
71. J.L. Braun, K.M. Holtman, J.F. Kadla, *Carbon* **43**, 385 (2005)
72. K. Sudo, K. Shimizu, *J. Appl. Polym. Sci.* **44**, 127 (1992)
73. J.M. Pickel, W.L. Griffith, A.L. Compere, *Abs. Pap. Am. Chem. Soc.* **231**, 133 (2006)
74. Y.H.P. Zhang, *J. Int. Microbio. Biotech.* **35**, 367 (2008)
75. W.M. Qiao, M. Huda, Y. Song, S.H. Yoon, Y. Korai, I. Mochida, O. Katou, H. Hayashi, K. Kawamoto, *Energ. Fuels* **18**, 2576 (2005)
76. N.M. Rodriguez, *J. Mater. Res.* **8**, 3233 (1993)
77. W. Xia, O.R.K. Schlüter, C. Liang, M.W.E. Berg, M. Curaya, M. Muhler, *Catal. Today* **102**, 34 (2005)
78. E. Hammel, X. Tang, M. Trampert, T. Schmitt, K. Mauthner, A. Eder, P. Pötschke, *Carbon* **42**, 1153 (2004)
79. G.T. Gary, *Carbon* **27**, 745 (1989)
80. R.M. Levit, *Khimicheskie Volokna* **6**, 16 (1990)
81. A. Ahmadpour, D.D. Do, *Carbon* **35**, 1723 (1997)
82. S.J. Park, B.J. Kim, *J. Colloid Interface Sci.* **282**, 124 (2005)
83. S.J. Park, J.S. Shin, J.W. Shim, S.K. Ryu, *J. Colloid Interface Sci.* **275**, 342 (2004)
84. S.J. Park, S.Y. Jin, *Carbon* **42**, 2113 (2004)
85. S.J. Park, B.J. Kim, *J. Colloid Interface Sci.* **291**, 597 (2005)
86. L. Giraldo, M.F. González-Navarro, J.C. Moreno-Piraján, *Carbon-Sci. Tech.* **5**, 303 (2013)
87. H.A. Al-Aoh, M.J. Maah, R. Yahya, M.R.B. Abas, *Asian J. Chem.* **25**, 9573 (2013)
88. Y.F. Li, Y. Liu, H.Q. Liu, L. Li, *Adv. Mater. Res.* **807–809**, 1343 (2013)
89. X. Ma, N. Li, J. Jiang, Q. Xu, H. Li, L. Wang, J. Lu, *J. Environ. Chem. Eng.* **1**, 466 (2013)
90. S. Shrestha, G. Son, S.H. Lee, T.G. Lee, *Chemosphere* **92**, 1053 (2013)
91. C.L. Lin, Y.H. Cheng, Z.S. Liu, J.Y. Chen, *J. Porus Mater.* **20**, 883 (2013)
92. A. Castro-Muñiz, F. Suárez-García, A. Martínez-Alonso, J.M.D. Tascón, T. Kyotani, *ChemSusChem* **6**, 1406 (2013)
93. C.H. Jung, I.H. Yoon, H.J. Woon, W.K. Choi, J.K. Moon, *Asian J. Chem.* **25**, 5602 (2013)
94. M.S. Berber-Mendoza, R. Leyva-Ramos, F.J. Cerino-Cordoba, J. Mendoza-Barron, H.J.A. Garcia, J.V. Flores-Cano, *Water Air Soil Pollut.* **224**, 1604 (2013)
95. W. Kempniński, D. Markowski, M. Kempniński, M. Śliwińska-Bartkowiak, *Carbon* **57**, 533 (2013)
96. H.A. Al-Aoh, M.J. Maah, R. Yahya, M.R.B. Abas, *Asian J. Chem.* **25**, 9582 (2013)
97. J. Yun, H.I. Kim, Y.S. Lee, *J. Mater. Sci.* **48**, 8320 (2013)
98. L. Huang, C. Shi, B. Zhang, S. Niu, B. Gao, *Sep. Sci. Technol.* **48**, 1356 (2013)
99. Y.C. Chiang, W.H. Lin, *Appl. Mech. Mater.* **284–287**, 72 (2013)
100. Y. Takahashi, H. Fujita, A. Sakoda, *Adsorption* **19**, 143 (2013)
101. C.A. Jeffs, M.W. Smith, C.A. Stone, C.G. Bezzu, K.J. Msayib, N.B. McKeown, S.P. Perera, *Micro. Meso. Mater.* **170**, 105 (2013)
102. J. Liu, Q. Zhou, J. Chen, L. Zhang, N. Chang, *Chem. Eng. J.* **215–216**, 859 (2013)
103. Z. Zhang, J.D. Atkinson, B. Jiang, M.J. Rood, Z. Yan, *Appl. Cat. B: Environ.* **148–149**, 573 (2014)
104. L. Sun, Y. Yao, L. Wang, Y. Mao, Z. Huang, D. Yao, W. Lu, W. Chen, *Chem. Eng. J.* **240**, 413 (2014)
105. F. Zhang, X.J. Ma, *Appl. Mech. Mater.* **469**, 117 (2014)

106. Y. Yao, V. Velpari, J. Economy, Fuel **116**, 560 (2014)
107. Z. Yue, C. Mangun, J. Economy, P. Kemme, D. Crokek, S. Maloney, Environ. Sci. Technol. **35**, 2844 (2001)
108. J.W. Shim, S.J. Park, S.K. Ryu, Carbon **39**, 1635 (2001)
109. S.J. Park, J.S. Shin, J. Colloid Interface Sci. **264**, 39 (2003)
110. S.J. Park, Y.M. Kim, Mater. Sci. Eng., A **391**, 121 (2005)
111. S.Y. Lee, S.J. Park, J. Colloid Interface Sci. **389**, 230 (2013)
112. J.S. Im, S.J. Park, Y.S. Lee, Mater. Res. Bull. **44**, 1871 (2009)
113. J.S. Im, S.J. Park, T.J. Kim, Y.S. Lee, Int. J. Hydrogen Energy **34**, 3382 (2009)
114. M.J. Jung, J.W. Kim, J.S. Im, S.J. Park, Y.S. Lee, J. Ing. Eng. Chem. **15**, 410 (2009)
115. S.J. Park, B.J. Kim, Y.S. Lee, M.J. Cho, Int. J. Hydrogen Energy **33**, 1706 (2008)
116. S.Y. Lee, H.M. Yoo, S.W. Park, S.H. Park, Y.S. Oh, K.Y. Rhee, S.J. Park, J. Solid State Chem. **215**, 201 (2014).
117. M. Foston, G.A. Nunnery, X. Meng, Q. Sun, F.S. Baker, A. Ragauskas, Carbon **52**, 65 (2013)
118. M.S. Morales, A.A. Ogale, J. Appl. Polym. Sci. **130**, 2494 (2013)
119. M. Speiser, S. Henzler, U. Hageroth, A. Renfflten, A. Müller, D. Schawaller, B. Sandig, M. R. Buchmeiser, Carbon **63**, 554 (2013)
120. A. Diaz, M. Guizar-Sicairos, A. Poepfel, A. Menzel, O. Bunk, Carbon (2013), Article in press
121. S.C. Bennett, D.J. Johnson, Strength-structure relationship in PAN-based carbon fibers, 5th London international carbon and graphite conference, society chemical industrial, London (1978)
122. D.L. Chung, *Carbon Fiber Composites; Butterworth-Heinemann: Boston* (Massachusetts, USA, 1992)
123. J.G. Morley, *High-Performance Fiber Composites* (Academic Press, Orlando, 1987)
124. W. Johnson, W. Watt, Nature **215**, 384 (1967)
125. X. Bourrat, E.J. Roche, J.G. Lavin, Carbon **28**, 435 (1990)
126. A. Oberlin, Carbon **22**, 521 (1984)
127. <http://www.toray.com/>
128. <http://www.tohotenax.com/>
129. <http://www.m-kagaku.co.jp/>
130. <http://www.hexcel.com/>
131. <https://www.cyttec.com/>
132. <http://www.fpcusa.com/>