

Chapter 2

Precursors and Manufacturing of Carbon Fibers

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Abstract In this chapter, we will present the precursors and manufacturing of carbon fibers. Among the precursors used for the production of carbon fibers, polyacrylonitrile (PAN)-based and pitch-based precursors are the most important. A significant amount of work has been done on relating the fiber structure to the properties and translating that relationship into production for either reducing cost or increasing fiber properties. However, challenges, including cost reduction, improvement in tensile and compressive strength, and alternative precursor development, still remain. We will also introduce many linear and cyclic polymers for carbon fibers, which is expected to open the door for the low-cost carbon fibers.

2.1 Introduction

Carbon fibers are novel high-performance materials. They could be described as fibers containing at least 90 % carbon obtained by the controlled pyrolysis of appropriate fibers. Edison in 1879 found that carbon fibers can be used as carbon filaments in electric lamps. Since the early work of Edison, the carbon fibers have been investigated and used intensively because they generally have excellent tensile properties, low densities, high thermal and chemical stabilities in the absence of oxidizing agents, good thermal and electrical conductivities, and excellent creep resistance [1–16].

In recent years, the carbon fiber industry has been growing steadily to meet the demands arising from different applications such as aerospace (aircraft and space systems), military, turbine blades, construction, lightweight cylinders and pressure vessels, medical, automobile, and sporting goods. Furthermore, in the case of the carbon fibers, the range of their applications would depend on the type of precursors used to produce the carbon fibers. Consequently, many types of precursors have been studied to produce the carbon fibers. The ideal features of precursors required

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to manufacture carbon fibers are easy conversion to carbon fiber, high carbon yield, and cost-effective processing. From this perspective, the following four types of precursors have been widely used, which have also proven to be the most popular ones [17–31]:

1. **Acrylic precursors:** They have been successfully used for carbon fiber preparation by most industrial manufacturers for quite some time now. These acrylic precursors contain >85 % acrylonitrile (AN) monomer. In particular, polyacrylonitrile (PAN) is the most popular acrylic precursor, which is used widely to produce the carbon fibers.
2. **Cellulosic precursors:** They contain 44.4 % carbon. However, in practice, the reaction is more complicated than mere dehydration, and the carbon yield is only approximately 25–30 %.
3. **Pitch-based precursors:** They have a yield of 85 %, and the resultant carbon fibers from these precursors show a high modulus owing to the more graphitic nature. On the other hand, the pitch-based carbon fibers have poorer compression and transverse properties compared to the PAN-based carbon fibers.
4. **Other forms of precursors:** Vinylidene chloride and phenolic resins as precursors for the manufacture of carbon fibers have been investigated, but were not found to be commercially viable.

2.2 Acrylic Precursors

Various acrylic precursors have been utilized to produce carbon fibers for use in carbon-fiber-based composite applications owing to certain desirable physical properties [32, 33]. The acrylic precursors for the carbon fiber industry originated from the companies that were established commercial-scale producers of textile-grade acrylic fibers. This was because the carbon fibers were produced through the pyrolysis of the acrylic fibers. Therefore, the manufacturers of carbon fibers could most readily adapt the existing technology for precursors to manufacture carbon fibers. The manufacturing processes of acrylic precursors by various manufacturers are listed in Table 2.1. In particular, the resultant carbon fibers from acrylic precursors such as PAN-based carbon fibers have been widely used as reinforcing materials in automobile, aerospace, recreational, and various other industries [34–37].

2.2.1 PAN Precursors

PAN-based polymer precursors for carbon fibers could be primarily classified into pure homopolymer and comonomers. Generally, the comonomers are widely used in PAN-based polymer precursors to manufacture carbon fibers [38–40].

Table 2.1 Manufacturing processes for acrylic precursors

Manufacturers	Trade name	Type of polymerization	Solvent	Typical % of polymer
Accordis	Courtelle	Continuous solution	NaCNS	10–15
Asahi	Cashmilon	Continuous aqueous dispersion	H ₂ O/HNO ₃	8–12
Hexcel	Exlan	Continuous aqueous dispersion	H ₂ O/ NaCNS	10–15
Mitsubishi	Finel	Continuous aqueous dispersion	H ₂ O/ DMAC	22–27
Toho	Beslon	Continuous solution	ZnCl ₂	8–12
Toray	Toraylon	Batch solution	DMSO	20–25

The homopolymer PAN product is slightly difficult to process into carbon fibers because the initial oxidation stage of the process cannot be easily controlled owing to the sudden and rapid evolution of heat, coupled with a relatively high initiation temperature. Such heat could result in poor properties of carbon fibers owing to the chain scission from the thermal shock. It is known that the homopolymer PAN product has never been used as a precursor for manufacturing carbon fibers. To overcome the resultant poor properties in the carbon fibers due to the rapid evolution of heat, the exothermic reaction should be adequately controlled using suitable comonomers such as itaconic acid.

On the other hand, as mentioned above, the comonomers could exert a significant effect on the stabilization process, thereby enhancing the segmental mobility of the polymer chains resulting in better orientation and mechanical properties of the precursor and manufactured carbon fibers. In addition, the selection of suitable comonomers could reduce the initial temperature of cyclization in the manufacturing process of carbon fibers. Therefore, several researchers have discussed the effect of comonomer composition on the properties of the PAN precursor and resultant carbon fibers.

Vinyl esters such as vinyl acetate (VAc), methacrylate (MA), and methyl methacrylate (MMA) could be used as comonomers for AN, though VAc might not be an appropriate carbon fiber precursor [41–44]. These comonomers act like a plasticizer and break up the structure to make the polymer more readily soluble in the spinning solvent, thereby improving the quality of spinning, modifying the fiber morphology and where appropriate, and improving the rate of diffusion of the dye into the fibers. However, the comonomers should be minimally used for establishing good properties in the carbon fibers because they could affect the cyclization step in the manufacturing process of carbon fibers. Table 2.2 lists the possible comonomers. These monomers have similar reactivities, and the resulting polymer compositions will have more or less the same composition as the monomers in the feed.



Carboxylic acids could be used as effective comonomers because their presence affects the ease of oxidation, exothermicity, and carbon yield of the precursor. In addition, itaconic and methacrylic acids have been confirmed to be most effective

Table 2.2 Comonomers for PAN precursors

Class	Comonomer	Structure
Acids	Acrylic acid	$\text{CH}_2=\text{CHCOOH}$
	Itaconic acid	$\text{CH}_2=\text{C}(\text{COOH})\text{CH}_2\text{COOH}$
	Methacrylic acid	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$
Vinyl esters	Methyl acrylate	$\text{CH}_2=\text{CHCOOCH}_3$
	Ethyl acrylate	$\text{CH}_2=\text{CHCOOC}_2\text{H}_5$
	Butyl acrylate	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{CH}_3$
	Methyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$
	Ethyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$
	Propyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{CH}_3$
	Butyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{CH}_3$
	β -Hydroxyethyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OH}$
	Dimethylaminoethyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
	2-Ethylhexylacrylate	$\text{CH}_2=\text{CHCOOCH}_2(\text{C}_2\text{H}_5)(\text{CH}_2)\text{CH}_3$
	Isopropyl acetate	$\text{CH}_3\text{COOC}(\text{CH}_3)=\text{CH}_2$
	Vinyl acetate	$\text{CH}_3\text{COOCH}=\text{CH}_2$
	Vinyl propionate	$\text{C}_2\text{H}_5\text{COOCH}=\text{CH}_2$
Vinyl amides	Acrylamide	$\text{CH}_2=\text{CHCONH}_2$
	Diacetone acrylamide	$\text{CH}_2=\text{CHONHC}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$
	N-methylolacrylamide	$\text{CH}_2=\text{CHONHCH}_2\text{OH}$
Vinyl halide	Allyl chloride	$\text{CH}_2=\text{CHCH}_2\text{Cl}$
	Vinyl bromide	$\text{CH}_2=\text{CHBr}$
	Vinyl chloride	$\text{CH}_2=\text{CHCl}$
	Vinylidene chloride (1,1-dichloroethylene)	$\text{CH}_2=\text{CHCl}_2$
Ammonium salts of vinyl compounds	Quaternary ammonium salt of aminoethyl-2-methylpropenoate	$\text{CH}_2=\text{CH}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{NH}_2$
Sodium salts of sulfonic acids	Sodium vinyl sulfonate	$\text{CH}_2=\text{CHSOONa}$
	Sodium p-styrene sulfonate (SSS)	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{SO}_3\text{Na}$
	Sodium methallyl sulfonate (SMS)	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{SO}_3\text{Na}$
	Sodium-2-acrylamido-2-methylpropane sulfonate (SAMPS)	$\text{CH}_2=\text{CHCONH}(\text{CH}_2)_3\text{SO}_3\text{Na}$

(continued)

Table 2.2 (continued)

Class	Comonomer	Structure
Others	Methacrylonitrile	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$
	2(1-Hydroxylalkyl) acrylonitrile	$\begin{array}{c} \text{CH}_2=\text{C}-\text{X} \\ \\ \text{R}-\text{CHOH} \end{array}$ (where R = $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$ and X = $-\text{CN}$ or $-\text{COOH}$)
	Allyl alcohol	$\text{CH}_2=\text{CHCH}_2\text{OH}$
	Methallyl alcohol	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$
	1-Vinyl-2-pyrrolidone	
	4-Vinylpyridine	$\text{HC}=\text{CH}_2$ 
	2-Methylene glutaronitrile	$\text{NCCCH}_2\text{CH}_2\text{C}=\text{CH}_2\text{CN}$

comonomers for reducing the exothermicity. Previous studies involving acrylic acid, acrylamide, sodium acrylate, and different acidic comonomers confirmed that the effectiveness of comonomers was in the following order: itaconic acid > methacrylic acid > acrylic acid > acrylamide [40]. The superiority of itaconic acid results from the presence of two carboxylic acid groups, which increases the possibility of interacting with a nitrile group. In other words, if one carboxylic acid group of itaconic acid moved away from an adjacent nitrile group owing to the dipole–dipole repulsion, the other carboxylic acid group could move into the vicinity of a nitrile group, thereby facilitating participation in the cyclization process [45, 46].

2.2.2 Polymerization Methods for Production of PAN-Based Precursors

Acrylic precursors such as AN and comonomers are initiated by free radical reaction and can be polymerized by one of the several methods listed below:

1. **Solution polymerization:** This method is used to prepare AN and comonomers by dissolving a monomer and catalyst in a nonreactive solvent. During this reaction, the solvent absorbs the heat generated by the chemical reaction and controls the reaction rate. The solvent used in the polymerization process usually remains as a solvent for the acrylic precursors (reactant). This process is only suitable for the creation of wet polymer types because the excess solvent is difficult to remove. During this reaction, the solvent absorbs the heat generated

by the chemical reaction and controls the reaction rate. The solvent used in the polymerization process usually remains as a solvent for the acrylic precursors (reactant). This process is only suitable for the creation of wet polymer types because the excess solvent is difficult to remove. Although the removal of excess solvent is possible using distillation, this method is usually not commercially viable. This polymerization method for the preparation of PAN-based precursors offers a few advantages as along with one major disadvantage [47].

2. Bulk polymerization: This method is the simplest and direct way of synthesizing polymers. This polymerization is carried out by adding a soluble initiator to a pure, liquid monomer. The initiator dissolves in the monomer, and the reaction is initiated by either heating or exposure to radiation. The mixture becomes viscous as the reaction proceeds. At that instant, the reaction is exothermic and a reactant with a broad molecular weight distribution is produced. Therefore, this polymerization method for the preparation of PAN-based precursors is used in the small-scale manufacturing process, wherein it is easy to remove the reaction heat [48].
3. Emulsion polymerization: This method is a type of radical polymerization, which is usually carried out with an emulsion containing water, monomer, and surfactant. The PAN-based precursors are often made commercially using emulsion polymerization [49].
4. Aqueous dispersion polymerization: This method is useful to prepare micro- or submicron-scale monodisperse polymer particles in a single step. In this polymerization method, all reaction materials are dissolved in the reaction medium in the initial stage of the polymerization. Then, insoluble spherical polymer particles, stabilized using steric molecules, are formed and dispersed in the reaction medium. PAN-based precursors could be prepared using this polymerization method with an ionic monomer to attain a narrow particle size distribution with a mean diameter as low as approximately $3 \pm 1.5 \mu\text{m}$ [50].

2.2.3 Manufacture of Carbon Fibers from PAN-Based Precursors

As mentioned earlier, the PAN-based polymers are the optimum precursors for the carbon fibers owing to a combination of tensile and compressive properties as well as the carbon yield. The PAN-based fibers were first developed by Dupont in the 1940s for use in the textile fiber. The thermal stability of PAN-based fibers was an important factor in expanding the application of fibers. Later, this property led to further research on the heat treatment of PAN fibers. In the early 1960s, PAN fibers were first carbonized and graphitized by Shindo at the Government Industrial Research Institute, Osaka, Japan, and these, in the early 1960s, PAN fibers were first carbonized and graph 112 GPa, respectively [51]. The process involved employing tension in both stabilization and carbonization steps. According to

Toray, Shindo's patent was licensed to Toray in 1970 by the Japanese Ministry of International Trade and Industry (MITI) to produce PAN-based Torayca carbon fibers. During the 1960s, Watt and Johnson at the Royal Aircraft Establishment, England, and Bacon and Hoses at Union Carbide, the USA, also developed a method for producing carbon fibers from PAN [52–54].

The manufacturing steps for producing the carbon fibers from PAN could be categorized as follows as shown in Fig. 2.1: polymerization of PAN-based precursors, spinning of fibers, thermal stabilization, carbonization, and graphitization. The manufacturing steps for producing the carbon fibers from PAN-based precursors could be categorized as follows as shown in Fig. 2.1: polymerization of PAN-based precursors, spinning of fibers, thermal stabilization (oxidation), carbonization, and graphitization Fig. 2.1. In addition, these PAN-based copolymers containing 2–15 % acrylic acid, methacrylic acid, MA, and/or itaconic acid are generally used as precursors of carbon fibers produced through carbonization because the use of comonomers affects the molecular alignment and stabilization conditions. The typical carbon yield from PAN-based precursors is approximately 50–60 % [55].

The typical manufacturing steps involved in the production of carbon fibers from PAN-based precursors are listed below:

1. Polymerization of PAN-based precursors and spinning of fibers

The PAN polymer precursor has been widely used as the basic backbone of chemical structure for spinning precursor fibers. Figure 2.2 shows the chemical structure of PAN. In addition, the commercial PAN-based polymer precursors used for spinning the precursor fibers usually contain approximately 2–10 % of a comonomer such as methyl acrylate (MA), MMA, or itacon acids (ITA). Most carbon companies manufacture their own precursors by in-house technologies. Consequently, the composition of the PAN polymer precursor is not well known because it can control the properties of the final products.

Generally, the PAN polymer precursors contain polar nitrile groups and have a high melting point, resulting from strong intermolecular interactions. Therefore,

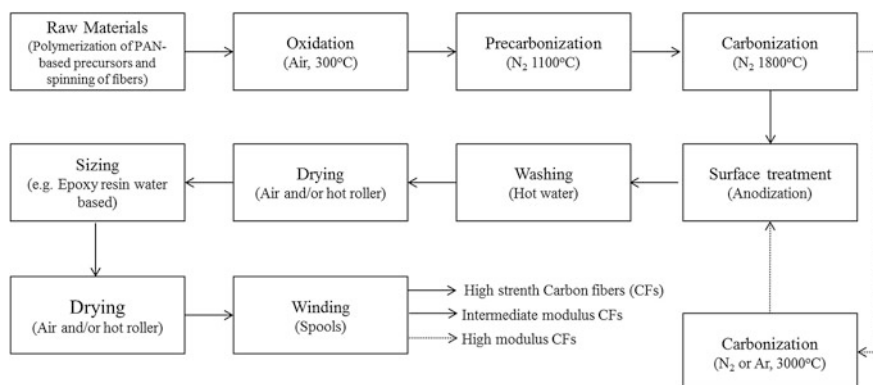
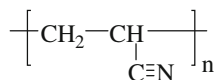


Fig. 2.1 Schematic for manufacturing process of carbon fibers from PAN-based precursors

Fig. 2.2 Chemical structure of PAN

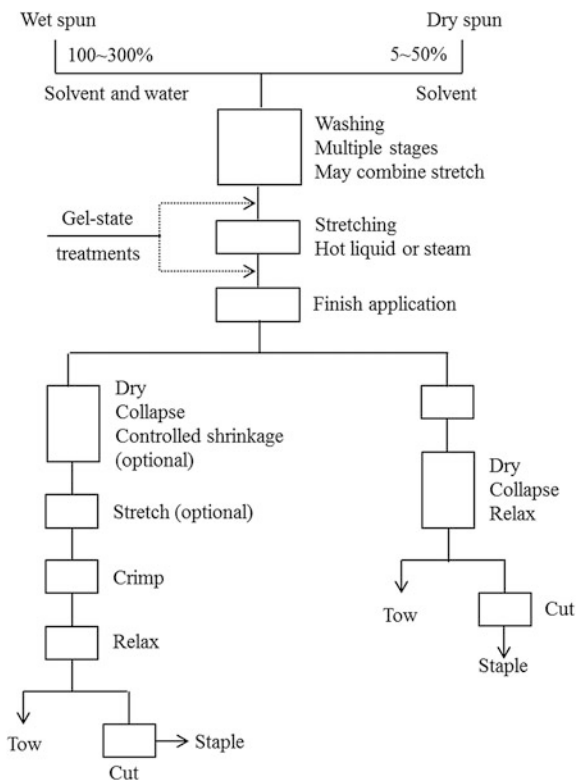


the PAN polymer precursors tend to degrade before the temperature reaches their melting point. The spinning of PAN fibers in the carbon fiber industry is performed using traditional manufacturing techniques of acrylic textile fibers. Wet spinning is used in most of the commercial manufacturing processes of carbon fibers produced from PAN-based polymer precursors. However, it is gradually being replaced by dry jet wet (air gap) spinning [56]. The melt spinning of PAN-based polymer precursors has been previously practised; however, it has yet to become an acceptable manufacturing process of carbon fibers, commercially [57–59]. Figure 2.3 shows the typical layout of a plant for processing PAN-based fibers.

2. Thermal stabilization (oxidation)

This process is critical to obtaining high-quality carbon fibers and could take up to several hours, depending on the temperature, precursor diameter, and precursor fiber characteristics [60–70]. Proper conditions such as heating rate, time,

Fig. 2.3 Typical layout of a plant for processing PAN-based fibers



and temperature of heating should be established for the optimum stabilization of each precursor. The PAN-based polymer precursor is stabilized by controlled low-temperature heating over the range 200–300 °C in air to convert the precursor to a form, which could be further heat-treated without either the melting or fusion of the fibers [71].

In this process, the linear molecules of PAN-based polymer precursor are first converted into cyclic structures. However, the cyclization is a complicated process, the mechanism of which is still unclear. In general, the most widely known reaction mechanism is shown in Fig. 2.4.

3. Carbonization and graphitization

The carbonization and graphitization of thermally stabilized fibers are carried out in an inert atmosphere containing gases such as nitrogen (N₂) or Ar [72]. Generally, N₂ is the preferred gas, but Ar is used despite being eight times more expensive. This is because Ar provides improved strength to the carbon fiber owing to the higher density and viscosity of argon. The temperature of carbonization is usually determined by the type of application of the resulting carbon fibers. For high-strength applications, the carbonization temperature over the range 1,500–1,600 °C is preferred because at temperatures above 1,600 °C, a decrease in the tensile strength occurs. On the other hand, an additional heat treatment above 1,600–1,800 °C and up to 3,000 °C, i.e., graphitization process, is required to obtain a high modulus in the carbon fibers [73, 74]. Nitrogen cannot be used at temperatures above approximately 2,000 °C owing to its reaction with carbon to form cyanogen. The heating rate and retention time during carbonization are different depending on the type of the precursor and stabilization conditions. Figure 2.5 shows the typical tensile strength (GPa) of the PAN-based carbon fibers depending on maximum carbonization temperature.

As mentioned above, the carbonization and graphitization of the thermally stabilized fibers is a two-step process, i.e., low-temperature carbonization and high-temperature graphitization, depending on the requisite properties of the carbon fibers. Bromley et al. [75] confirmed that the gases evolved during the carbonization of PAN-based carbon fibers over the low-temperature range 200–1,000 °C, and the observed gases are listed in Table 2.3.

Figure 2.6 shows the schematic of the graphite structure. Dehydrogenation joined the ladder molecules to form graphite-like ribbons; however, denitrogenation made the ribbons to form sheet-like structures. On the other hand, the high carbonization temperature caused the ordered structure to grow in both thickness and area, increased the crystalline orientation in the fiber direction,

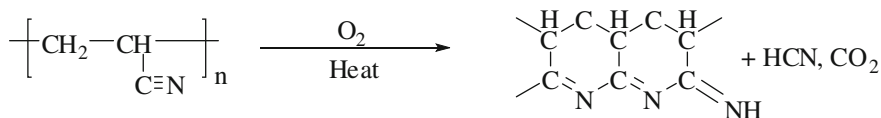


Fig. 2.4 Mechanism of cyclization of PAN polymer precursor

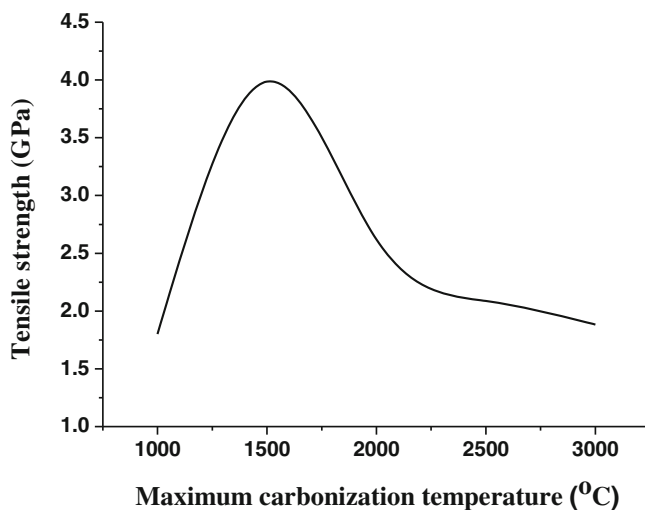
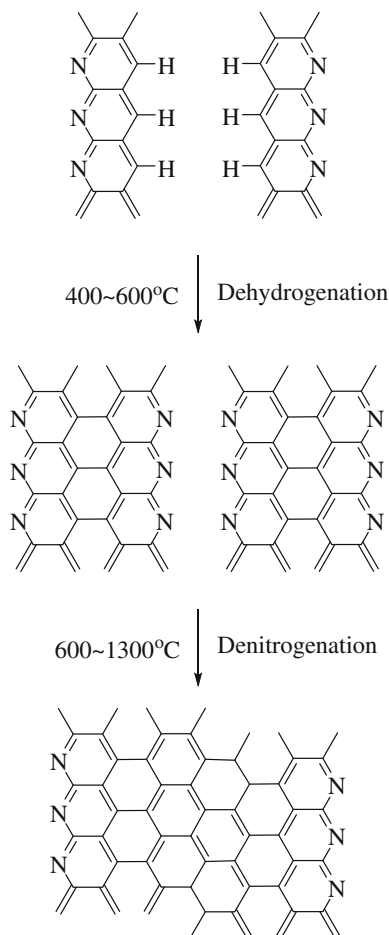


Fig. 2.5 Typical tensile strength (GPa) of PAN-based carbon fibers depending on maximum carbonization temperature

Table 2.3 Gases evolved during carbonization of PAN-based carbon fibers

Temperature (°C)	Observation	Interpretation
220	HCN evolved and O ₂ chemically bonded	Ladder polymer formation and oxidation of polymer
260	Little changed. No modulus increased	No chain scission
300	Large CO ₂ and H ₂ O evolution; also CO, HCN, and some nitriles. No modulus increased	CO ₂ from –COOH groups in oxidized polymer No cross-linking
400	CO ₂ , H ₂ O, CO, HCN, and NH ₃ evolved. Small evolution of C3 hydrocarbons and nitriles Modulus increased	Cross-linking by intramolecular H ₂ O elimination
500	Increased H ₂ evolution. Some NH ₃ and HCN evolved. Modulus increased	Cross-linking by dehydrogenation
600	Reduced H ₂ evolution. HCN and trace N ₂	Cross-linking by dehydrogenation
700	N ₂ , HCN, and H ₂ evolution. Modulus increased	Cross-linking by dehydrogenation and evolution of N ₂
800	Large increase in N ₂ , H ₂ , and HCN still evolved. Modulus increased	Cross-linking by evolution of N ₂
900	Maximum evolution of N ₂ , some H ₂ , and traces of HCN. Modulus increased	Cross-linking by N ₂ elimination
1,000	N ₂ evolution decreases to approximately the same level as that at 800 °C. Trace H ₂ evolved. Modulus increased	Cross-linking by N ₂ elimination

Fig. 2.6 Schematic of graphite structure



and reduced the interlayer spacing and void content. In addition, the graphite structures could further grow at higher temperatures resulting from the elimination of N_2 .

4. Surface treatment and washing

Generally, the surface treatment of carbon fibers was performed to improve the mechanical properties of the composite through alteration of the fiber surface. In many companies, the treatment method of the surface of carbon fibers is still kept confidential. The most often used surface treatment methods for carbon fibers could be categorized as liquid and gaseous oxidation treatments. The liquid oxidation treatment is well known and could double the composite shear strengths with slight reductions (4–6 %) in fiber tensile strengths [76].

Among the oxidation treatment methods of the liquid type, the anodic oxidation treatment method has been widely used in the surface treatment of commercial carbon fibers because it is inexpensive, fast, and efficient. Figure 2.7 shows the

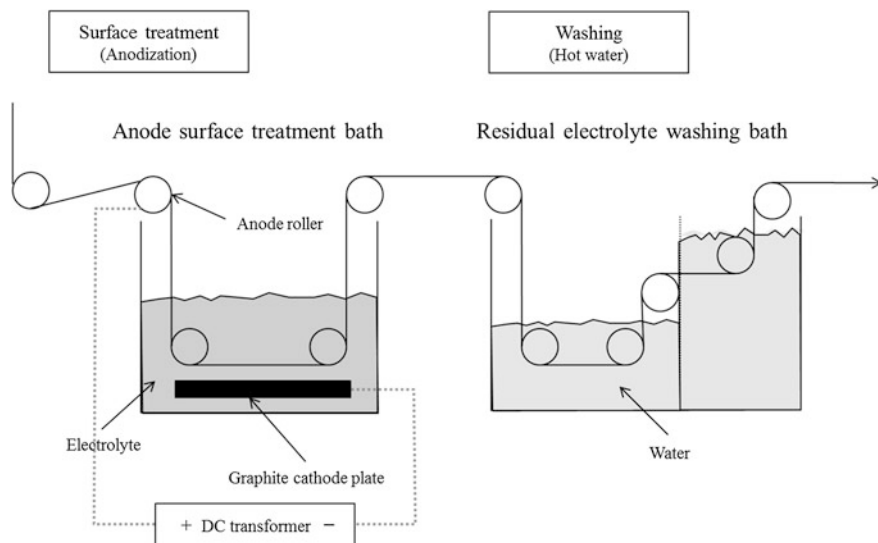


Fig. 2.7 Schematic of surface treatment and washing baths

schematic of the surface treatment and washing baths. In this method, Faraday's Law applies and 96,500 C liberates 1 g equivalent of O_2 . The duration of the surface treatment is related to the line speed. In addition, the current density as a standard variable is used to control the treatment level per unit length of carbon fiber during the surface treatment, usually expressed as C/m.

The electrically conductive carbon fibers form the anode during the electrolysis of an acid or a salt solution such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), ammonium sulfate ($(NH_4)_2SO_4$), and ammonium bicarbonate (NH_4HCO_3) [77]. One of the electrolytes, ammonium sulfate, is usually used in the commercial surface treatment processes of carbon fibers. This causes the carbonyl containing groups such as COOH to form on the smooth fiber surface. The carbonyl groups improve the cohesion between the fiber and resin used in the final composite. After this surface treatment, the excess electrolyte is removed using warm water wash treatment. The carbon fibers are then passed onto the next process through one or more water baths constantly flowing with water.

Currently, the demand for the surface treatment of carbon fibers has significantly increased with increasing necessity for high-performance carbon fiber composites.

5. Drying, sizing, and winding

Carbon fibers require some protection or lubrication for the ease of handling because of their brittleness. The carbon fibers are predried for the sizing treatment, and the sizing materials are selected such that they protect the physical characteristics of carbon fibers. These sizing materials need to provide consistent handling and not build up residue on the processing equipment. The sizing

materials also need to be compatible with the matrix resin. This includes solubility in and/or reactivity with the formulated resin. This allows the resin to penetrate the fiber bundle and interact with the fiber surface. Generally, the epoxy resins or epoxy formulations are used as sizing materials. The sizing materials should not change either the chemical or physical characteristics of the carbon fibers during storage. Some sizing materials are water soluble and washable after either weaving or braiding [78].

The fiber sizing, process to apply sizing, and sizing content are considered to be critical factors in the carbon fiber specification. The type of size material and particle size of the aqueous dispersion must be controlled to establish good properties in the carbon fibers after sizing. From these viewpoints, the types of emulsifier and resin and their respective concentrations are key to improving the characteristics of the carbon fibers. The control of wetting in the sizing bath is needed to control the level of size on the carbon fibers. All the steps pertaining to the application of the sizing to the carbon fiber and drying must also be consistent (Fig. 2.8).

Many sizing materials such as epoxy resins are not soluble in water and must be applied as a dispersion or emulsion in water. This could result in the sizing being uniformly distributed on the surface of the fibers. Alternately, the sizing materials could exist as either droplets on the fiber surface or by sticking together a number of individual fibers. The particle size of the emulsion in the sizing bath is controlled to provide a dependable product.

Meanwhile, the dried carbon fibers after the sizing treatment are collected using winders. The winding machines generally operate automatically. In addition, the winders could usually produce finished spools of up to 12 kg in weight.

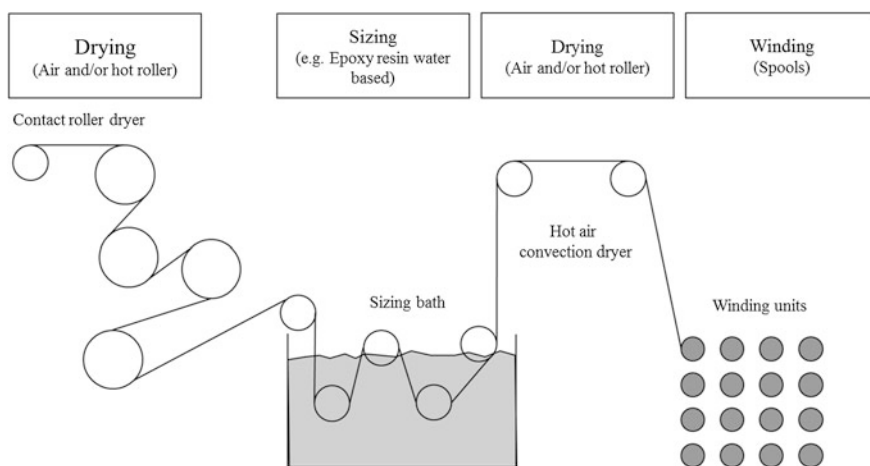


Fig. 2.8 Schematic of drying, sizing, and winding

2.2.4 Types of Polyacrylonitrile-Based Carbon Fibers

There are three basic categories of PAN-based carbon fibers:

1. Large tow: Inexpensive to manufacture can be conveniently chopped to a staple form
2. General purpose grades: Less stringent product qualification
3. Aerospace grades: Premium-grade products

Each category of carbon fibers is available in several production types, which are based on their tensile strength and modulus:

- general purpose
- high strength
- intermediate modulus
- high modulus

2.3 Cellulosic Precursors

2.3.1 Cellulosic Precursors

Cellulose as a precursor for making carbon fibers was first used by Thomas Edison in the 1880s for his revolutionary electric lamp filament. Almost 80 years later, in 1959, the National Carbon Company (a division of Union Carbide) produced a carbon cloth from a rayon precursor, and two years later, in 1961, a carbon yarn was introduced [79]. In 1965, Thornel series—carbon fibers with a tensile strength of 1.25 GPa and a Young's modulus of 170 GPa—was introduced [80]. The properties of these carbon fibers were improved by postcarbonization treatment involving stretching at 2,500 °C. However, the production of these carbon fibers was delayed by more than 10 years because of the high cost of the heat stretching process, lower yield, and properties of the cellulose precursor.

Ford and Mitchell [81] proposed a process, which could be used for rayon monofilaments, cellulosic yarns, or prewoven rayon textile material. Their process involved a controlled heating process comprising heating at 10 °C/h up to 100, 50 °C/h up to 400 and 100 °C/h up to approximately 900 °C, followed by heating up to 3,000 °C until the graphitization had occurred. A protective atmosphere of nitrogen or other inert gases was used when heating over the range 900–3,000 °C. The resultant carbon fibers from this process showed improved tensile strength compared to the earlier carbon fibers. Furthermore, the stronger graphitic structure in these carbon fibers was confirmed using X-ray patterns [82, 83].

Tang and Bacon [84] proposed the four simplified stages mentioned below for the conversion of cellulose to carbon:

1. Stage I: Physical desorption of approximately 12 % absorbed water (25–150 °C) with a small degree of change in the lateral order.
2. Stage II: Dehydration from the –H and –OH fragments present in the cellulose unit (150–240 °C). IR shows that –C = O and –C–C– are involved, and hence, dehydration is essentially intramolecular.
3. Stage III: Thermal cleavage of the glycosidic linkage and scission of other C = O and some C–C bonds via a free radical reaction (240–400 °C) which leads to the formation of large amounts of tar, H₂O, CO and CO₂.
4. Stage IV: Aromatization (400 °C and above), wherein each cellulose unit breaks down into a residue containing four C atoms, which then polymerize through condensation reactions involving the removal of –H above 400 °C into a C-polymer with a graphite-like structure.

Strong [85] described the small-scale heat treatment of rayon precursors for stress graphitization. Because stress graphitization was to be accomplished at approximately 2,800 °C, any nonuniformity in the yarn could lead to either a nonuniform stretch or breakage during the stretching process. Therefore, it was essential that the fiber be well supported and transported by rollers. The rayon textile finish was removed by extraction with boiling water, and as far as could be ascertained, no flame resistant finish was applied.

The pyrolysis process was undertaken with either: (i) a continuous treatment for approximately 7 min in oxygen at 260–280 °C or (ii) a batch treatment for approximately 20 h in air at 225 °C with 40 % weight loss, followed by 7 min in O₂ to afford a total weight loss of 50–55 %. To initiate the development of the final carbon structure and sufficiently improve the strength to enable stress-carbonization, treatment in N₂ for 1.5 min at 350 °C was carried out. The material was carbonized over the range 900–2,000 °C and graphitized over the range 2,800–2,900 °C. X-ray diffraction studies showed that the starting material Cellulose II was converted to the Cellulose IV structure before degradation commenced. It was observed that during pyrolysis in air, shrinkage occurred at approximately 25–45 % weight loss, associated with a tendency to kink if the yarn was not under tension. So, the pyrolysis stage was deliberately limited to postpone the second weight loss stage to the carbonization step, during which sufficient tension could be applied to prevent kinking.

2.3.2 Rayon Precursor for Production of Cellulose-Based Carbon Fibers

Cellulose is a promising precursor for carbon fiber production. In addition, through pyrolysis, it forms strong carbon fibers, and the cellulosic precursors have high thermal conductivity, high purity, mechanical flexibility, and low precursor cost [86]. The regenerated cellulose fiber precursors used to make carbon fibers are viscose, cuprammonium rayon, or rayon textile-grade rayon.

1. Viscose rayon [87]

The process of manufacturing viscose rayon consists of the following steps mentioned, in the order in which they are carried out: (1) steeping, (2) pressing, (3) shredding, (4) aging, (5) xanthation, (6) dissolving, (7) ripening, (8) filtering, (9) degassing, (10) spinning, (11) drawing, (12) washing, and (13) cutting. The various steps involved in the process of manufacturing viscose are shown in Fig. 2.9.

(1) Steeping

Cellulose pulp is immersed in 17–20 % aqueous sodium hydroxide (NaOH) over the temperature range 18–25 °C to swell the cellulose fibers and convert the cellulose to alkali cellulose.

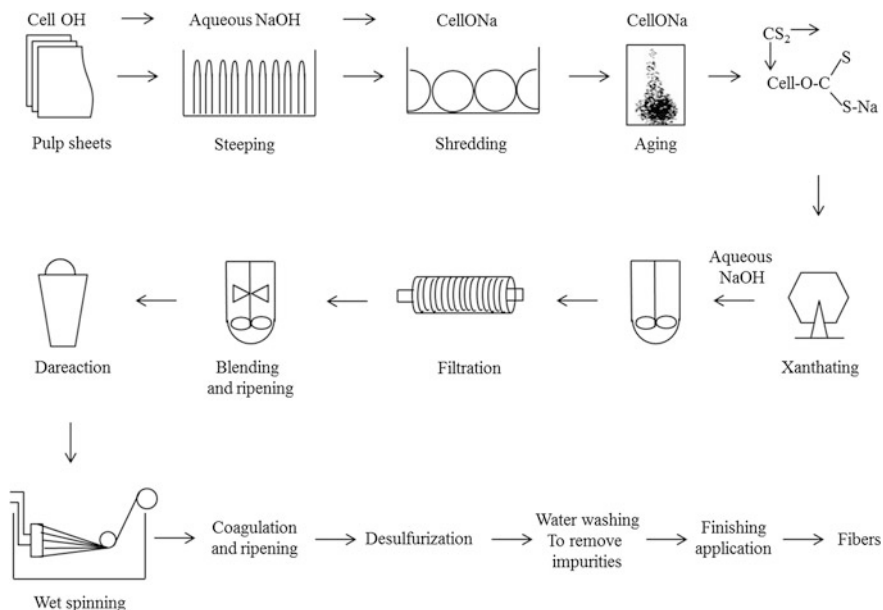
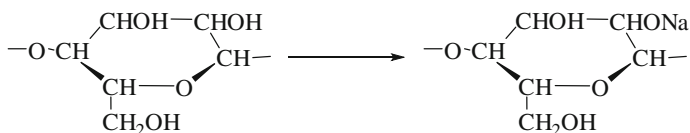
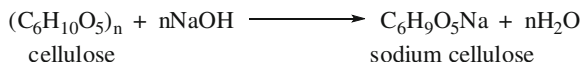


Fig. 2.9 Process of manufacture of viscose rayon fibers

(2) Pressing

The swollen alkali cellulose mass is pressed to a wet weight equivalent of 2.5–3.0 times the original pulp weight to obtain an accurate ratio of alkali to cellulose.

(3) Shredding

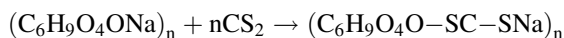
The pressed alkali cellulose is shredded mechanically to yield finely divided, fluffy particles called “crumbs.” This step provides increased surface area of the alkali cellulose, thereby increasing its ability to react in the steps that follow.

(4) Aging

The alkali cellulose is aged under controlled conditions of time and temperature (between 18 and 30 °C) in order to depolymerize the cellulose to the desired degree of polymerization. In this step, the average molecular weight of the original pulp is reduced by a factor of two to three. The reduction of the cellulose is done to get a viscose solution of right viscosity and cellulose concentration.

(5) Xanthation

In this step, the aged alkali cellulose crumbs are placed in vats and are allowed to react with carbon disulfide under controlled temperature (20–30 °C) to form cellulose xanthate.



Side reactions, which occur along with the conversion of alkali cellulose to cellulose xanthate, are responsible for the orange color of the xanthate crumb as well as the resulting viscose solution. The orange cellulose xanthate crumb is dissolved in dilute sodium hydroxide at 15–20 °C under high-shear mixing conditions to obtain a viscous orange colored solution called “viscose,” which is the basis for the manufacturing process. The viscose solution is then filtered (to remove the insoluble fiber material) and deaerated.

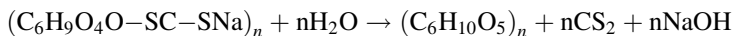
(6) Dissolving

The yellow crumb is dissolved in an aqueous caustic solution. The large xanthate substituents on cellulose force the chains apart, reducing the interchain hydrogen bonds and allowing water molecules to solvate and separate the chains, thereby leading to a solution of the otherwise insoluble cellulose. Because of the blocks of the unxanthated cellulose in the crystalline regions, the yellow crumb is not completely soluble at this stage. Because the cellulose xanthate solution (or more accurately, suspension) has high viscosity, it has been termed “viscose.”

(7) Ripening

The viscose is allowed to stand for a period of time to “ripen.” Two important processes occur during ripening: redistribution and loss of xanthate groups. The reversible xanthation reaction allows some of the xanthate groups to revert to the cellulosic hydroxyls and free CS₂. This

free CS_2 can then either escape or react with other hydroxyls on other portions of the cellulose chain. In this way, the ordered, or crystalline, regions are gradually broken down, and a more complete solution is achieved. The CS_2 , which is lost, reduces the solubility of the cellulose and facilitates the regeneration of the cellulose after it is formed into a filament.



(8) Filtering

The viscose is filtered to remove the undissolved materials, which might either disrupt the spinning process or cause defects in the rayon filament.

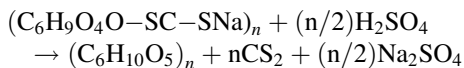
(9) Degassing

Bubbles of air entrapped in the viscose must be removed prior to extrusion, or else, they cause voids, or weak spots, in the fine rayon filaments.

(10) Spinning (Wet Spinning)

Production of Viscose Rayon Filament: The viscose solution is metered through a spinneret into a spin bath containing sulfuric acid (to acidify the sodium cellulose xanthate), sodium sulfate (to impart a high salt content to the bath, which is useful in the rapid coagulation of viscose), and zinc sulfate (for exchange with sodium xanthate to form zinc xanthate, to cross-link the cellulose molecules). Once the cellulose xanthate is neutralized and acidified, a rapid coagulation of the rayon filaments occurs, followed by simultaneous stretching and decomposition of cellulose xanthate to regenerated cellulose. The stretching and decomposition processes are vital for obtaining the desired tenacity and other properties of rayon. The slow regeneration of cellulose and stretching of rayon leads to greater areas of crystallinity within the fiber, as is done with high-tenacity rayon.

The dilute sulfuric acid decomposes the xanthate and regenerates cellulose by wet spinning. The outer portion of the xanthate is decomposed in the acid bath, forming a cellulose skin on the fiber. Sodium and zinc sulfates control the rate of decomposition (of cellulose xanthate to cellulose) and fiber formation.



Elongation-at-break is seen to decrease with increasing degree of crystallinity and orientation of rayon.

(11) Drawing

The rayon filaments are stretched, while the cellulose chains are still relatively mobile. This causes the chains to stretch out and orient along the fiber axis. As the chains become more parallel, the interchain

hydrogen bonds form, providing the filaments with the properties necessary for use as textile fibers.

(12) Washing

The freshly regenerated rayon contains many salts and other water soluble impurities, which need to be removed. Several different washing techniques may be used.

(13) Cutting

If the rayon is to be used as staple (i.e., discrete lengths of fiber), the group of filaments (termed “tow”) is passed through a rotary cutter to yield a fiber, which can be processed analogously to cotton.

2. Cuprammonium rayon [88]

In this process, the fibers are produced in a solution of cellulosic material in cuprammonium hydroxide at a low temperature in nitrogen atmosphere, followed by extruding through a spinneret into a sulfuric acid solution, necessary to decompose the cuprammonium complex to cellulose. This is a relatively more expensive process than that used for viscose rayon. However, the cross sections of the resultant fibers are almost round (Fig. 2.10).

3. Saponified cellulose acetate rayon [88, 89]

Rayon can be produced from cellulose acetate yarns through saponification. Purified cotton is steeped in glacial acetic acid to make it more reactive. It is then acetylated with an excess of glacial acetic acid and acetic anhydride, followed by sulfuric acid to promote the reaction. The cellulose triacetate formed by acetylation is hydrolyzed to convert the triacetate to diacetate. The resultant mixture is poured into water, which precipitates the cellulose acetate. For spinning, it is dissolved in acetone, filtered, deaerated, and extruded into hot air, which evaporates the solvent. A high degree of orientation can be given to the fiber by drawing because cellulose acetate is more plastic. Its fiber cross section is nearly round, but lobed (Fig. 2.11).

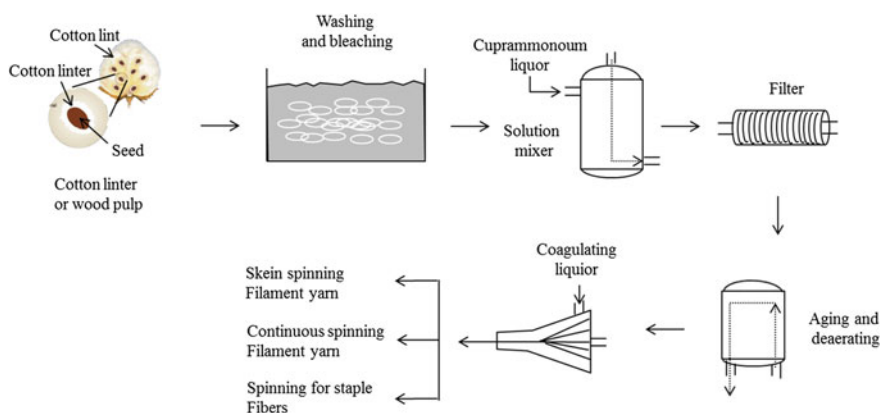


Fig. 2.10 Process of manufacture of cuprammonium rayon fibers

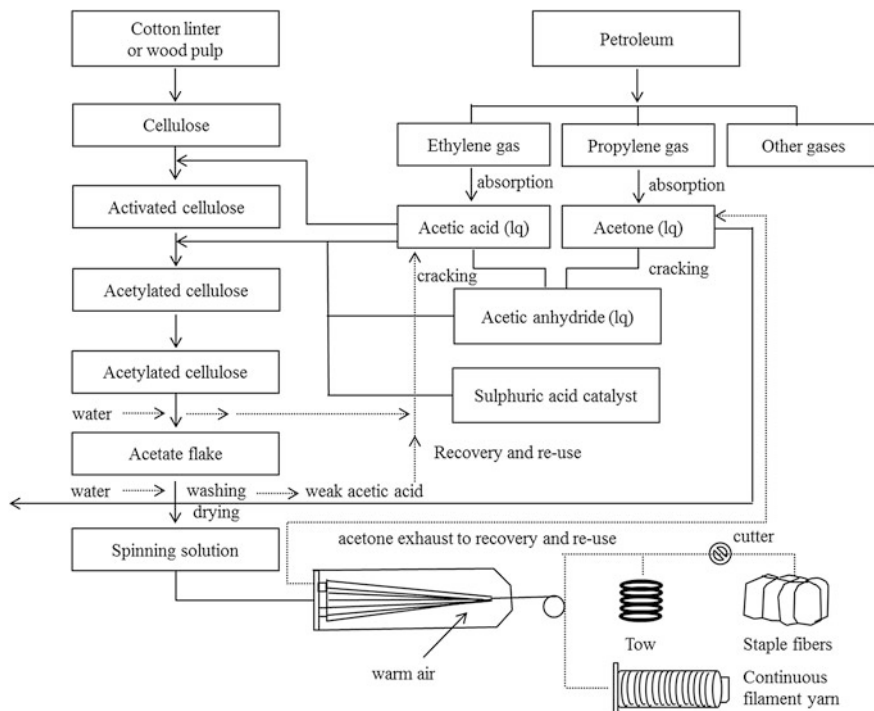


Fig. 2.11 Process of manufacture of saponified cellulose acetate rayon

2.3.3 Manufacture of Carbon Fibers from Cellulosic Precursors

Rayon fibers, as mentioned above, can be converted into carbon fibers with chemical, physical, mechanical, and microstructural changes, through stabilization and carbonization processes. With regard to chemical and mechanical properties, the stabilization of the precursor fibers is important to produce stable carbon fibers through the subsequent carbonization process. In particular, the thermal shrinkage of the cellulose fibers occurs owing to the weight reduction of fibers during the stabilization process [90]. Therefore, in this section, only the stabilization, carbonization, and graphitization of cellulosic precursors for manufacturing of carbon fibers will be described. Other processes such as surface treatment, sizing, and winding are identical to the processing of the PAN-based carbon fibers.

1. Stabilization

Cellulose is a glucose-based, linear polymer connected by β -(1-4) glycosidic linkages (Fig. 2.12). The hydroxyl groups can easily form intra- and intermolecular hydrogen bonds in the cellulose structure, and the hydrogen bonds can lead to various ordered crystalline arrangements. From the molecular

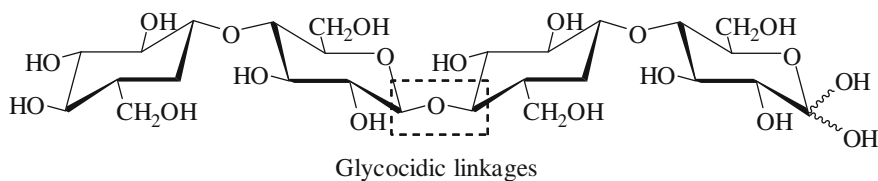


Fig. 2.12 Chemical structure of cellulose polymer chain

stoichiometry of $(C_6H_{10}O_5)_n$, it was found that the theoretical carbon yield of the carbonization process for the cellulosic structure is 44.4 %. However, the actual carbon yield is only between 10 % and 30 %, resulting from the depolymerization of the macromolecular chains and the elimination of carbon by oxygen in the forms of carbon monoxide (CO), carbon dioxide (CO_2), aldehydes, organic acids, and tars. Therefore, the selection of suitable stabilizer materials is essential for improving the carbon yield and properties of the products in the carbonization process, which can lead to higher efficiency [91–94].

The degradation of general cellulose fibers under an inert atmosphere initiates at 200 °C and ends at around 380 °C. In addition, the thermal stability of the cellulose sources depends on the process conditions for cellulose fiber production. Although the physicochemical processes taking place during the transformation of cellulose into carbon are complex, it is certain that the depolymerization of the macromolecular chains produces a variety of oxygenated compounds. This leads to the major mass loss of the solid residue through the production of volatile substances. Various methods can help in reducing the burning loss. One method involves the modification of cellulose precursors to improve the yield and properties of the carbon fibers. The other method involves the pyrolysis of the cellulose with slow heating rates of a few °C/h or the treatment of cellulose fibers with suitable impregnators [95, 96].

The pyrolysis of cellulose is mainly controlled by two predominant reactions, dehydration and depolymerization (cleavage) (Fig. 2.12). The main reaction at low temperatures (300 °C) is the dehydration reaction for the stabilization of the cellulose structure. During the dehydration, the elimination of the hydroxyl groups leads to conjugated double bonds, and subsequently, the dehydrated cellulose ring becomes less accessible for cleavage compared to the original cellulose structure in an aromatic form in the carbonization step. The polymeric structure is basically retained through dehydration, and the weight loss at this temperature range is usually owing to the evaporation of water. Depolymerization in the early stages of pyrolysis with the incomplete dehydration of the cellulose structure causes major mass loss at higher temperatures. Therefore, a slow heating rate of a few °C/h can be used to increase the carbon yield of the cellulose fibers. In addition, the slow pyrolysis influences the properties of the final fibers such as improved density, porosity, and microstructure, compared to fast pyrolysis [97].

2. Carbonization and graphitization

As shown in Fig. 2.13, the first H_2O dehydration occurs between 25 and 150 °C (Stage I), and the physical desorption of water and dehydration of the cellulosic unit occur between 150 and 240 °C (Stage II). This leads to the formation of the double-bonded intermediates [98]. Carbonization of cellulose refers to the conversion process from this depolymerized structure into graphite-like layers through repolymerization. The process begins at approximately 300 °C and continues up to 900 °C, as shown in the Stages III and IV of Fig. 2.13. The basic microstructure of the carbon is formed during the Stage III [82]. As shown in Fig. 2.13, the thermal cleavage of the glycosidic linkage and the scission of ether bonds occur over the range 240–400 °C. Moreover, depolymerization to monosaccharide derivatives occurs during this stage of carbonization. Then, these intermediates form aromatic structures, releasing gases containing non-carbon atoms (O, H) [99]. The carbonaceous residue is converted into a more ordered carbon structure through heat treatment between 400 and 900 °C under an inert atmosphere. The full mechanism of aromatization related to the graphitic products is still unknown, owing to the complex characterization of the cellulose decomposition and existence of many competing reactions during the different stages of carbonization.

The heat treatment up to 900 °C causes the formation of semiordered carbonaceous structures under an inert atmosphere. After this stage, the carbonized fibers can be treated with heat at higher temperatures to initiate graphitization. In general, graphitization is carried out under stress at 900–3,000 °C to obtain high-modulus fibers through the development of an enhanced order of the graphene stacks, both laterally between the layers (crystallographic register) and in terms of the preferred orientation along the fiber axis. The Young's modulus is increased by the increasing treatment temperature, if the graphitization is conducted under tension. After graphitization, the carbon content of the fibers usually increases to above 99 %, and the fiber density increases resulting from the growth of crystallites [100].

2.4 Pitch Precursors

Pitches are complex blends of polyaromatic molecules and heterocyclic compounds, which can be used as precursors of carbon fibers or carbon fillers in carbon composites. These pitches can contain more than 80 % carbon, and the composition of a pitch varies with the source tar and processing conditions [101]. In addition, these pitches can be obtained from one of several sources mentioned below:

1. Petroleum refining, normally called bitumen, or asphalt
2. Destructive distillation of coal
3. Natural asphalt, e.g., from Trinidad
4. Pyrolysis of PVC

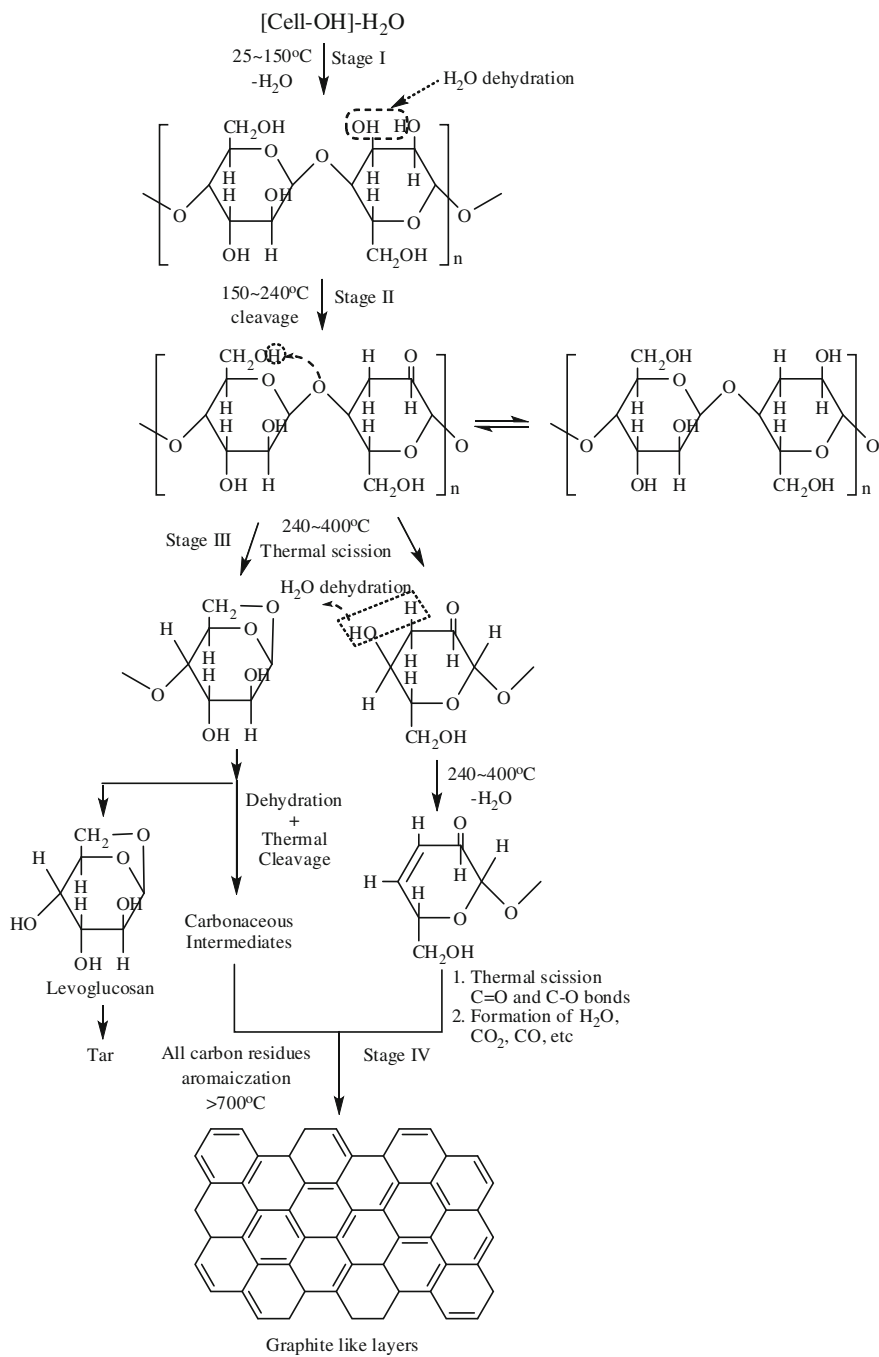


Fig. 2.13 Reactions involved in conversion of cellulose into carbon fibers

Table 2.4 Compositions of various oils and pitches

Compound	Asphaltene (%)	Polar aromatic (%)	Naphthene aromatic (%)	Saturate (%)	Softening point (°C)
Carbon black oil	2.5	10.6	69.0	17.9	
EXXON (DAU) bottoms (refinery sludge)	14.5	41.1	18.1	26.3	29
Ashland 240 petroleum pitch	64.4	8.6	25.4	1.6	119
Ashland 260 petroleum pitch	82.7	5.9	11.4	0.0	177

As mentioned above, the natural pitches are produced by the refining of petroleum and destructive distillation of coal, while the synthetic pitches are produced by the pyrolysis of synthetic polymers. Generally, among the prepared pitches using several sources, the petroleum pitch and coal pitch are widely used in the production of carbon fibers [102].

In terms of the components of pitch, Riggs et al. considered that the pitch is composed of four main classes of chemical compounds [103].

1. Saturates: Low molecular weight aliphatic compounds
2. Naphthene aromatics: Low molecular weight aromatics and saturated ring structures
3. Polar aromatics: Higher molecular weight and more heterocyclic in nature
4. Asphaltenes: Highest molecular weight fraction in pitch with the highest aromaticity and thermally most stable

The compositions of various oils and pitches are listed in Table 2.4. Several researchers have confirmed that the asphaltene-rich materials are the most suitable for conversion into carbon fibers.

2.4.1 Petroleum Pitch Precursors

Petroleum pitch can be obtained from various sources such as heavy residue obtained from a catalytic cracking process and steam cracker tar—a by-product of the steam cracking of naphtha or gas oils to produce ethylene or any residues from crude oil distillation or refining [104]. Many methods can be used for the production of pitch and are based on an initial refining process, which can include either one method or combination of several treatment methods listed below:

1. Prolonged heat treatment to advance the molecular weight of the components
2. Air bowing at approximately 250 °C
3. Steam stripping and application of vacuum to remove low boiling components
4. Distillation

In common with the coal tar pitch, the chemical and physical characteristics of petroleum pitch are dependent on the process and conditions employed, especially the process temperature and heat treatment time. Generally, longer times and higher temperatures produce pitches with increased aromaticity and higher anisotropic contents. The petroleum pitches are usually less aromatic compared to the coal tar pitch [105].

2.4.2 Coal Tar Pitch Precursors


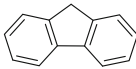
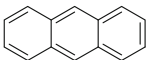
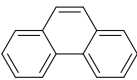
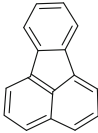
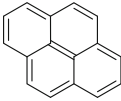
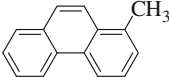
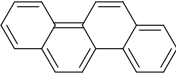
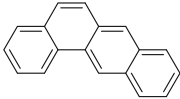
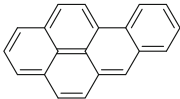
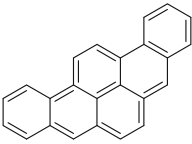
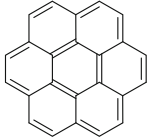
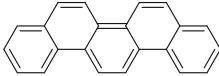
Coal tar is a by-product of the coking of bituminous coals to produce cokes [106]. The metallurgical cokes are produced at high temperatures (between 900 and 1,100 °C), but it produces smokeless fuels at lower temperatures (approximately 600 °C). The low-temperature process affords a smaller amount of tar compared to the high-temperature process. Coal tar pitch is obtained from the coal tar using distillation and heat treatment processes. The pitch is the residue, which follows the removal of the heavy (creosote or anthracene) oil fractions. The pitches are complex mixtures containing many different individual organic compounds, and the precise compositions and properties vary according to the source of the tar and method of removal of low molecular weight fractions. Smith et al. [107] and Guigon et al. [108] reported that roughly two-thirds of the compounds isolated hitherto from the coal tar pitch are aromatic, and the rest are heterocyclic. Most of the compounds are substituted with the methyl group. The majority of the coal tar pitch components contain between three and six rings, having boiling points over the range 340–550 °C. Table 2.5 lists the major aromatic hydrocarbon compounds, which have been quantitatively found in a typical coal tar pitch [106–109].

2.4.3 Preparation Methods of Pitch-Based Precursors

1. Preparation methods of petroleum pitch

Many petroleum products are referred to as “pitch” by the petroleum industry. This could cause considerable confusion outside the refining community. In most cases, the different types of petroleum pitch exist as black solids at room temperature. The individual characteristics of the petroleum pitches vary with the functions of the feedstock and specific processes used in their manufacture. Feedstock can range from being predominantly aliphatic to predominantly aromatic-type chemical structures. A reaction step is used to generate and/or concentrate the large molecules typically observed in petroleum pitch. The most common processes used to generate petroleum pitches are either singular processes or a combination of: (a) solvent deasphalting, (b) oxidation, and (c) thermal processes [110].

Table 2.5 Aromatic hydrocarbon components present in coal tar pitch

			
Acenaphthene	Fluorene	Anthracene	Phenanthren
			
Fluoranthene	Pyrene	Methylphenanthrene	Chrysene
			
Benz-(a)-anthracene	Benzo-(a)-pyrene	3, 4, 8,10-Dibenzopyrene	
			
Coronene	Picene		

Solvent deasphalting is used to separate the fractions of various heavy oils. It involves mixing the feedstock with a paraffinic solvent such as propane, butane, or pentane. The mixing of the feedstock with these light paraffinic solvents causes the precipitation of molecules with higher molecular weights and aromaticities. The chemical and physical properties of this type of petroleum pitch are more closely associated with the asphalt cements used for paving roads. Typical properties include specific gravity of approximately 1.0 g/cc at 60 °F, with the chemical composition containing significant amounts of nonaromatic hydrocarbons and high levels of iron, nickel, and vanadium [111].

Various grades of pitch can be produced by the oxidation of heavy petroleum hydrocarbons. Although oxygen is used in the process, the products typically do not contain significant amounts of oxygen. During this reaction, the presence of

oxygen is successful in generating free radicals, which induce the polymerization reactions. The chemical properties of these products will depend upon the starting material and degree of reaction, but the pitches produced typically have low coking values and high viscosities [112].

Thermal processing is used to produce the petroleum pitch, as noted in several patents. Thermal processing has traditionally been used to produce the high specific gravity and aromatic petroleum pitches referred to in the introduction of this chapter. The thermal processes typically employ heat treatment temperatures over the range 300–480 °C. A typical schematic for producing the petroleum pitch from crude oil using thermal processing is shown in Fig. 2.14.

2. Preparation methods of coal tar pitch

Coal tar is a by-product of the coking of coal, used to produce metallurgical coke [113]. Coal is heated to approximately 1,100 °C in a coke oven to produce coke (the primary product) and by-products such as coke oven gas, coal tar light oil, and coal tar. The typical yields are 70 % solid products and 30 % liquid products. The yield of coal tar, the feedstock for producing coal tar pitch, from a ton of coal is 30–45 L (8–12 gallons). Coal tar pitch has several uses, but the majority of the pitch produced is used as a binder for petroleum coke to produce

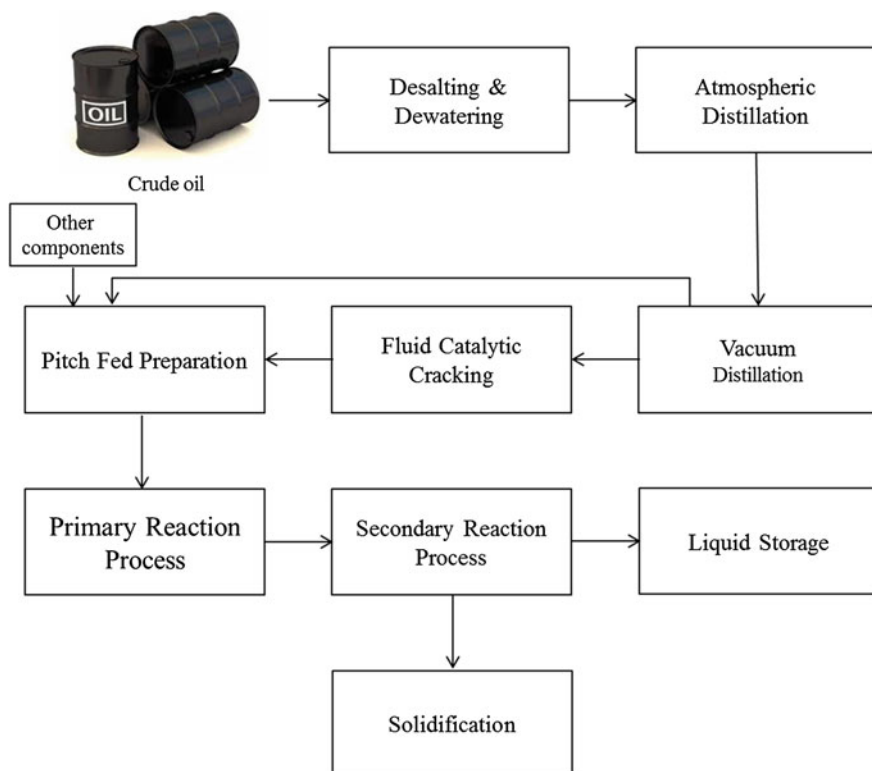


Fig. 2.14 Schematic for the manufacturing process of petroleum pitch from crude oil

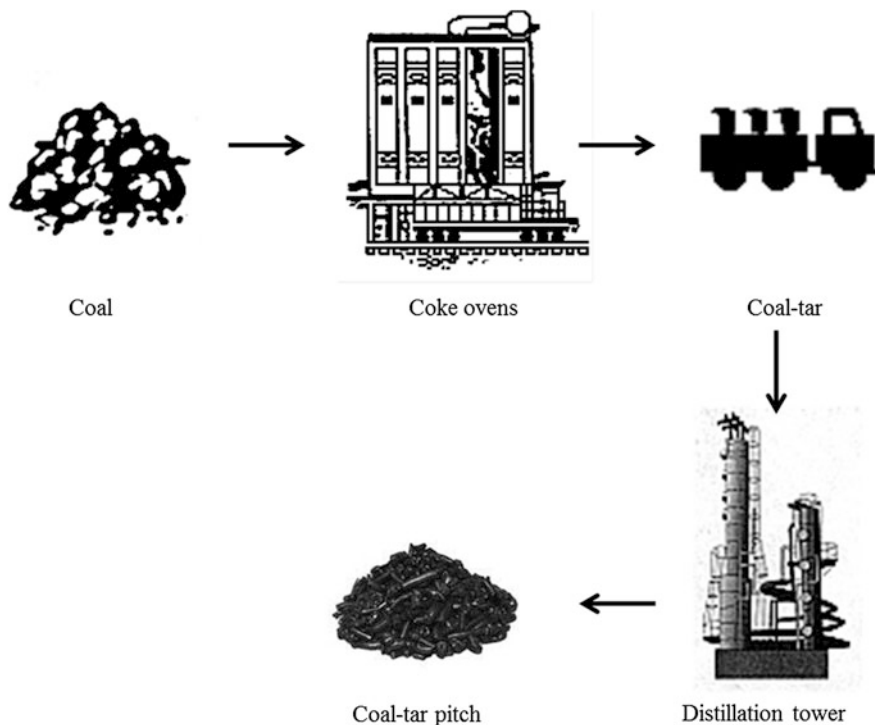


Fig. 2.15 Schematic for the manufacturing process of coal tar pitch

anodes and graphite electrodes [114]. Figure 2.15 shows the schematic for coal tar pitch production. As indicated in the figure, the coal tar pitch is produced by the distillation of coal tar.

Pitch as a precursor has the advantage of lower material cost, higher char yield, and higher degree of orientation compared to those of PAN [115]. The graphitic structure also affords pitch-based carbon fibers, higher elastic modulus, and higher thermal and electrical conductivity along the fiber direction [116]. However, the processing cost (mainly pitch purification, mesophase formation, and fiber spinning) to achieve high-performance carbon fibers is higher. The pitch from petroleum and coal tar is isotropic. By evaporating the low molecular weight fractions, the isotropic pitch can be melt-spun into low-cost general purpose (GP) (low strength and low modulus) carbon fibers. To produce high-performance fibers, an expensive hot stretching process (explained in the following section) needs to be applied. A more common method to produce high-performance carbon fibers from the pitch is to use an anisotropic pitch such as mesophase pitch [117].

1. Isotropic pitch

Isotropic pitches are used to make a GP grade of pitch carbon fibers, which are not graphitic and have poorer properties compared to the high-performance

grade (HP), which requires a special treatment process to convert the pitch to a mesophase grade, i.e., an optically anisotropic and graphitic material. The isotropic pitch has to be treated to generate a product suitable for melt spinning, with low volatility and filtered to remove the solid particles. A good starting material would be Ashland 240, which has low quinoline content. The volatile components can be effectively removed with a wiped film evaporator, wherein a thin film of the molten pitch in the evaporator is continuously wiped over the heating surface, exposing a fresh surface, thus permitting the efficient removal of some of the volatile components without overheating. Also, while the pitch is molten, any solid impurities are removed by filtration. These refining processes raise the softening point and avoid the formation of mesophase. Hence, increasingly, pitches such as Ashland's Aerocarb 60 and 70 can be used. The preparations of isotropic pitches have been undertaken to make GP carbon fibers [118, 119].

2. Mesophase pitch

The mesophase pitches used for high-modulus carbon fiber production can be formed either by the thermal polymerization of petroleum- or coal-tar-based pitches, or the catalytic polymerization of pure compounds such as naphthalene. The mesophase transformation results in an intermediate phase, formed between 400 and 550 °C, by the thermal treatment of aromatic hydrocarbons. During the mesophase formation, domains of highly parallel, plate-like molecules form and coalesce until 100 % anisotropic material may be obtained in due course. It has been well established that when the mesophase pitch is carbonized, the morphology of the pitch is the primary factor that determines the microstructure of the resulting graphitic material [120, 121].

The typical methods used for the production of the mesophase pitch are listed below:

- (1) pyrolysis of isotropic pitch
- (2) solvent extraction
- (3) hydrogenation
- (4) catalytic modification

2.4.4 Manufacture of Carbon Fibers from Pitch-Based Precursors

The production of carbon fibers from pitch-based precursors proceeds in several stages: production of precursor fibers, stabilization of the precursor fibers, carbonization of the stabilized precursor fibers, and graphitization of the carbonized precursor fibers. The stabilization process is the most important stage during which the thermal oxidation takes place in the precursor carbon fibers. Only properly stabilized precursor fibers can assure satisfactory performance of the final carbon

fiber product. Other processes such as surface treatment, sizing, and winding are identical to the processing of PAN-based carbon fibers.

The typical manufacturing steps for the production of carbon fibers from pitch-based precursors are listed below:

1. Production of precursor fibers by melt spinning [122]

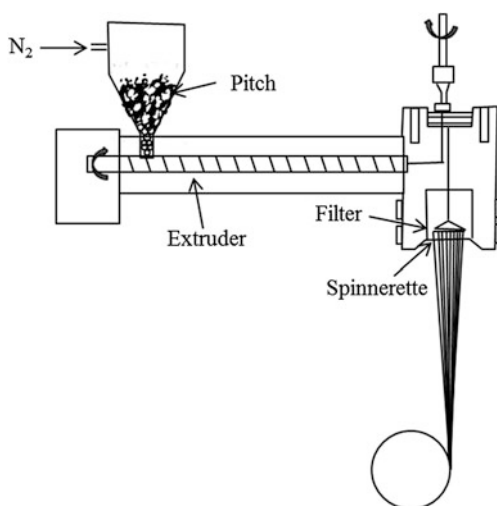
Melt spinning involves three steps: melting the precursor, extrusion through a spinneret capillary, and drawing the fibers as they cool. Many investigators have concluded that this process is the primary source of structure in the mesophase pitch-based carbon fibers and that thermal treatment only reinforces this structure. The effects of melt spinning conditions on the structure and properties of carbon fibers will be discussed in this section.

Several process variables are important in determining the fibers' potential for developing an ordered graphitic structure. The first is melt temperature. Each mesophase has a range of temperature over which the melt spinning is possible. Spinning at temperatures below this range results in high viscosities and brittle fracture during drawdown, while at temperatures above this range, thermal degradation of the pitch and dripping owing to low viscosity occur. The viscosities of all the mesophases are highly dependent upon temperature, as shown in Fig. 2.16; therefore, the temperature range for successful melt spinning is quite narrow. Using the AR mesophase, Mochida found that decreasing the melt spinning temperature by even 15° resulted in a fourfold increase in viscosity and, in turn, significant decreases in the tensile strength and Young's modulus. It was, therefore, concluded that a low melt viscosity was necessary for the production of high-quality carbon fibers.

2. Stabilization of precursor fibers

Analogous to the PAN precursor fibers, the pitch fibers are either infusibilized or oxidized in air at elevated temperatures before being exposed to the final high-

Fig. 2.16 Schematic of melt spinning process for production of precursor fibers



temperature carbonization treatment. The oxidization temperature should be below the fiber softening point to keep the orientated structure. Depending on the composition, the mesophase pitch precursor is stabilized in air at 250–350 °C for a duration ranging from 30 min to several hours. There has been no consensus hitherto on the purpose of the fiber stretching in this step. The oxidized pitch molecules contain ketone, carbonyl, and carboxyl groups, which lead to the stronger hydrogen bonding between the adjacent molecules. The introduction of oxygen containing groups and formation of hydrogen bonding between the molecules facilitate the three dimensional cross-linking, but hinder the growth of crystallites. Iodine has been used to reduce the stabilization time and increase the carbon yield of carbon fibers from the natural pitch. In a patent by Sasaki and Sawaki [123], the pitch fiber was soaked in a methanol solution of iodine till at least 0.05 wt. % of iodine was imbibed. The fiber was then heated under an oxidizing atmosphere for infusibilization. The infusibilization time was affected by the amount of imbibed iodine but generally could be completed within approximately 10 min [123, 124].

3. Carbonization and graphitization of stabilized precursor fibers

Stabilized fibers are then carbonized and graphitized. The greatest weight loss takes place in the early stages of carbonization. In order to avoid the defects created by the excessive release of volatiles, the fibers are precarbonized for a brief period of 0.5–5 min at 700–900 °C. The carbon fibers can be produced by carbonizing the stabilized fibers to 1,500–1,800 °C. Bright and Singer [125] reported that because of the degradation of the structure, the modulus decreased at temperatures up to approximately 1,000 °C, but increased significantly upon further increase in temperature. The carbon fibers can be graphitized at temperatures close to 3,000 °C for enhanced Young's modulus. Barr et al. [126] have shown that increasing the heat treatment temperature could increase the preferred alignment of the crystalline lamellae.

Although graphite layers are aligned along the fiber axis, the transverse structures of the carbon fibers can be different. The velocity gradients orient the layers radially, circumferentially, or randomly. It has been reported that a radial crack can form in the mesophase carbon fibers with layer planes distributed radially. The alignments in the precursor fiber are retained in the resultant carbon fiber. Therefore, carbon fiber strength could be improved by adjusting the microstructure in the precursor fiber. Research has shown that the flaw sensitivity of mesophase carbon fibers is reduced by varying the microstructure of the pitch precursor fibers. The microstructure can be modified by changing the flow profiles during melt spinning. A radial cross section is usually formed through the laminar flow of the pitch melt. Petoca Oil Company has employed agitation in the spinneret to impart a randomized distribution for the folded graphene layer planes in the transverse direction. The agitation created a turbulent flow and the resultant carbon fibers showed increased tensile strength. The turbulent flow can also be obtained by different die designs because the flow behavior heavily depends on the shape of the spinneret. Spinnerets containing

sections with different diameters have shown to be able to change the fiber microstructure. Because melt flow is dependent on melt viscosity, the change in the microstructure can also be obtained simply by changing the spinning temperature. Otani and Oya [127] have shown that when the spinning temperature was raised to above 349 °C, the radial structure changed to either a random type or radial type, surrounded by an onion-skin-type structure.

2.5 Other Forms of Precursors

Many other polymers have also been investigated for their potential as carbon fiber precursors [128–137]. In addition to the cellulosic fibers discussed earlier, other natural fibers have been investigated and considered as the precursors for carbon fibers such as silk, chitosan, and eucalyptus [128–136]. They can lower the production cost; however, most of them are used for GP carbon fibers, which do not afford strong mechanical properties.

In addition, many linear and cyclic polymers have been investigated as a precursor for the production of carbon fibers, including phenolic polymers, polyacene-naphthalene, polyamide, polyphenylene, poly-p-phenylene benzobisthiazole (PBBT), polybenzoxazole, polybenzimidazole, polyvinyl alcohol, polyvinylidene chloride, and polystyrene. Linear precursors require heat stretching to obtain high-performance carbon fibers, and their carbon yields are usually extremely low [137]. The polymers with high aromatic content can generally offer a high carbon yield and in some cases easy stabilization. However, these polymers either have high costs or do not produce high-performance carbon fibers. Further research needs to be conducted to reduce the processing cost while improving the mechanical properties of the resultant carbon fibers.

2.6 Summary

In this chapter, we have given a brief overview of the precursors and manufacturing of carbon fibers. Among the precursors used for the production of carbon fibers, PAN-based and pitch-based precursors are the most important. A significant amount of work has been done on relating the fiber structure to the properties and translating that relationship into production for either reducing cost or increasing fiber properties. However, challenges, including cost reduction, improvement in tensile and compressive strength, and alternative precursor development, still remain.

Many polymers such as linear and cyclic polymers have been evaluated as low-cost carbon fiber precursor materials. It will open the door for low-cost carbon fibers. However, more research needs to be conducted to optimize the processing conditions to enhance the mechanical properties and carbon yield of the resultant carbon fibers.

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