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Review article

A review of heat treatment on polyacrylonitrile fiber

M.S.A. Rahaman, A.F. Ismail*, A. Mustafa

Membrane Research Unit (MRU), Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, Skudai 81310, Johor, Malaysia

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Abstract

Developing carbon fiber from polyacrylonitrile (PAN) based fiber is generally subjected to three processes namely stabilization, carbonization, and graphitization under controlled conditions. The PAN fiber is first stretched and simultaneously oxidized in a temperature range of 200–300 °C. This treatment converts thermoplastic PAN to a non-plastic cyclic or a ladder compound. After oxidation, the fibers are carbonized at about 1000 °C in inert atmosphere which is usually nitrogen. Then, in order to improve the ordering and orientation of the crystallites in the direction of the fiber axis, the fiber must be heated at about 1500–3000 °C until the polymer contains 92–100%. High temperature process generally leads to higher modulus fibers which expel impurities in the chain as volatile by-products. During heating treatment, the fiber shrinks in diameter, builds the structure into a large structure and upgrades the strength by removing the initial nitrogen content of PAN precursor and the timing of nitrogen. With better-controlled condition, the strength of the fiber can achieve up to 400 GPa after this pyrolysis process.

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Keywords: Polyacrylonitrile; Heat treatment; Stabilization; Carbonization; Carbon fiber

1. Introduction

It has been documented that the majority of all carbon fibers used today are made from PAN precursor, which is a form of acrylic fiber. PAN which is a polymer with a chain of carbon connected to one another (Fig. 1) is hard, horny, relatively insoluble, and a high-melting material [1]. It has been established that PAN-based carbon fiber is stronger than other type of precursor-based carbon fiber [2]. PAN-based fibers also have been found to be the most suitable precursors for producing high performance carbon fibers (compared to pitch, rayon, etc.) generally because of its higher melting point and greater carbon yield (>50% of the original precursor mass) [3–7]. Although carbon fiber can be from pitch precursor, the processing and purifying it to the fiber form is very expensive and generally, they are more expensive than PAN-based fibers [8]. PAN with molecular formula $[C_3H_3N]_n$ can produce carbon fiber of relatively high carbon yield giving rise to

a thermally stable, extremely oriented molecular structure when subjected to a low temperature treatment [9]. PAN fiber was also preferred to be the precursor because of its fast rate in pyrolysis without changing its basic structure [9]. Optimizing the pyrolysis of PAN precursor fiber would ideally result in enhanced performance of the resulting carbon fiber.

Recent study has established that PAN fibers were used on a large scale in textile industry and one of the most suitable and widely applied for making high performance carbon fibers [10–13]. Most PAN-based carbon fibers extensively applied in last two decades were used in the composite technology [14]. They are highly desirable for high performance composites for automotive and aerospace technologies due to their enhanced physical and mechanical characteristics [9]. Fitzer [15] and Chen and Harrison [16] believed that the optimization of PAN fiber would ideally result in high performance for use in aerospace application. Hence PAN-based fiber that leads to a good balance in properties can be used in structural applications and provide high strength [2].

Year by year there will be an improvement on performance as well as strength and modulus of PAN-based carbon fiber

* Corresponding author. Tel.: +607 5535592; fax: +607 5581463.

E-mail address: afauzi@utm.my (A.F. Ismail).

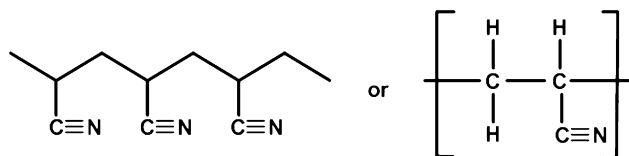


Fig. 1. Molecular structure of polyacrylonitrile.

[17]. Traceski [18] stated that the total worldwide production of PAN-based carbon fiber was 19 million lbs per year for 1989 and increased up to 26 million lbs per year. In addition, the worldwide outlook for the demand of PAN carbon fibers is currently amounting to a nearly \$6 billion pound per year worldwide effort [19,20]. So, the wide availability of PAN precursor had triggered the production of carbon fiber.

1.1. Heat treatment

Heat treatment is a process that converts the PAN fiber precursor to carbon fiber. Currently 90% of all commercial carbon or graphite fibers are produced by the thermal conversion of a PAN precursor, which is a form of acrylic fiber. The successful conversion of PAN to high strength, high modulus fibers depend in part upon the understanding of the oxidative and thermal treatment. Liu et al. [21] listed the three steps for the conversion of precursor of PAN-based fiber to carbon, which are as follows.

- i. Oxidative stabilization, which forms ladder structure to enable them to undergo processing at higher temperatures.
- ii. High temperature carbonization, ($\leq 1600\text{ }^{\circ}\text{C}$) to keep out noncarbon atoms and yield a turbostatic structure.
- iii. Further heat up to $2000\text{ }^{\circ}\text{C}$ to improve the orientation of the basal planes and the stiffness of fibers, which is called graphitization.

2. Precursor stabilization

Among the conversion processes shown in Fig. 2, an essential and time-consuming step in the conversion of PAN fibers to high performance carbon fiber is the oxidative stabilization step [7]. This can be explained by chemical reactions that are involved in this process, which are cyclization, dehydrogenation, aromatization, oxidation and crosslinking which can result in the formation of the conjugated ladder structure [22,23]. The oxidative stabilization stage is one of the most complicated stages, since different chemical reactions take place and the structure of the carbon fiber is set in this stage.

Stabilization process, which is done in atmosphere can change chemical structure of the fiber and cause them to become thermally stable and so melting will not reoccur [24]. Recently, the stabilization process is found to play an important role in converting PAN fiber to an infusible stable ladder polymer that converts $\text{C}\equiv\text{N}$ bonds to $\text{C}=\text{N}$ bonds [25] and to develop crosslink between molecules of PAN [26] which tend to operate at high temperatures, with minimum volatilization of carbonaceous material. The thermal stability of the stabilized fiber is attributed to the formation of the ladder structure due to

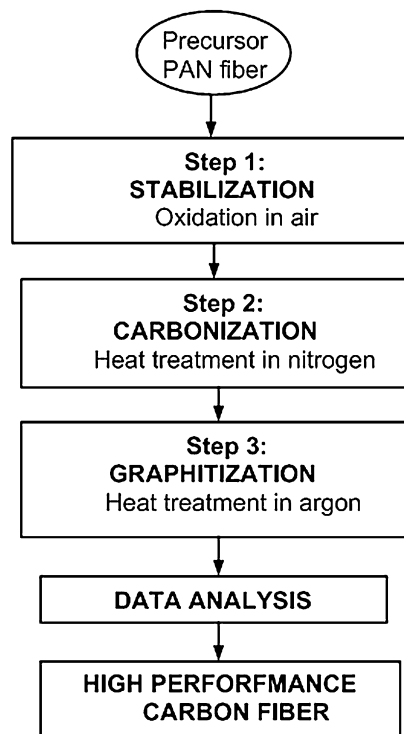


Fig. 2. PAN precursor carbon fiber conversion process.

cyclization of the nitrile groups in acrylic molecule. Setnescu et al. [27] observed that CH_2 and CN groups disappeared completely due to elimination, cyclization and aromatization reactions and formed $\text{C}=\text{C}$, $\text{C}=\text{N}$ and $=\text{C}-\text{H}$ groups. Typically, during the course of stabilization, the PAN-based precursor fiber undergoes a change in colour from white through shades of yellow and browns to ultimately a black stabilized fiber. The mechanism for colouration is not fully understood. However, the appearance of black colour is believed to be due to the formation of ladder ring structure [28,29].

In this process, the required temperature is the important factor that would affect the heating treatment of PAN fiber. Heat treatment involved in stabilization of PAN fiber is carried out usually at the region of $180\text{--}300\text{ }^{\circ}\text{C}$ [24,30]. When temperature exceeds $180\text{ }^{\circ}\text{C}$, the molecular chains will unfold and move around. But some researchers found that heating temperature within $200\text{--}300\text{ }^{\circ}\text{C}$ are usually used to stabilize the fiber [7,23,25,31–34]. Fitzer et al. [35] suggested that in producing best performance carbon fiber, the best stabilized temperature is $270\text{ }^{\circ}\text{C}$. However, other researchers [36–38] found that heating treatment needs higher than $300\text{ }^{\circ}\text{C}$ to complete the stabilization. Mathur et al. [39] also proposed that PAN fiber does not get preferred stability at $270\text{ }^{\circ}\text{C}$ but needs higher temperature up to $400\text{ }^{\circ}\text{C}$. It was known that PAN fiber with optimum stabilization condition can produce higher modulus carbon fiber than unstabilized fiber or than fiber which is prepared at high temperature stabilization process [31]. If the temperature is too high, the fibers can overheat and fuse or even burn. However, if the temperature is too low, the reactions are slow and incomplete stabilization can be resulted, yielding poor carbon fiber properties.

Previously two important reactions occur during stabilization process which can change the chemistry of PAN structure [40]. They are dehydrogenation and cyclization reactions as illustrated in Fig. 3. Both are important to form ladder polymer structure which was thermally stable and might be able to withstand high temperature during pyrolysis process. In addition, stabilization process also could be present in oxidation reaction which gives an insight about diffusion of oxygen through the reacting polymer [41].

2.1. Oxidation reaction

The oxidation reaction during PAN-based precursor stabilization is the least reaction and is the step which most precursors depend. Commercially, stabilization of PAN fiber is done in an ‘oxidizing’ medium which is typically air. The reaction exotherm when PAN is stabilized in air is partly due to reaction with oxygen. Although stabilization could be done in an inert atmosphere, a polymer back-bone containing oxygen-bearing groups that evolves in PAN ladder structure (Fig. 4) provides greater stability to sustain high temperature carbonization treatment [42].

Fitzer and Muller [43] have concluded that the activation energy and the frequency factor were greater in air than in nitrogen (inert gas). This indicates that oxygen is an initiator for the formation of activated center for cyclization because of the increase in the activation energy. Consequently, various structures of oxidized PAN that account for the presence of oxygen have been proposed including those containing bridging ether links, those containing carbonyl groups, and those in which each nitrogen atom donates its lone pair of electron to an oxygen (as shown in Fig. 5) [5,44].

2.2. Dehydrogenation process

Dehydrogenation is the formation of double bonds that stabilizes carbon chain and cyclization is the process by which

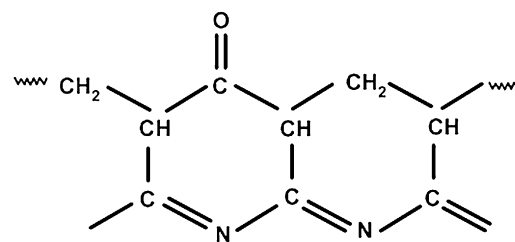


Fig. 4. Ladder PAN structure [26].

the rings are formed. The dehydrogenation reactions have at least two elementary steps, with oxidation in the first step and elimination of water in the second. Studies have shown that either the original PAN polymer or cyclized ladder polymer can undergo dehydrogenation [43]. As a conclusion from Fig. 3, the reactions are usually written in the form of Fig. 6. Since oxygen is required for the reaction to proceed, dehydrogenation does not occur in inert atmosphere. This is different from the cyclization reaction. The double bond or unsaturated bond that formed in the reaction improves the polymer’s thermal stability and reduces chain scission during carbonization [45].

2.3. Cyclization reaction

The last reaction that would be discussed is cyclization which is the most important reaction in the stabilization of PAN fiber. Cyclization is the reaction of the nitrile groups in the precursor polymer with adjacent groups to form a stable, ladder polymer and could be described by first order kinetic equation [43]. Cyclization is the most important reaction in stabilization process. The cyclization of the nitrile groups is an exothermic reaction and that the evolution of gaseous products accompanies this reaction [46]. The reaction is necessary to hold molecules in fiber together and increases the stiffness [47–50]. In addition, the idea of cyclization was conceived by

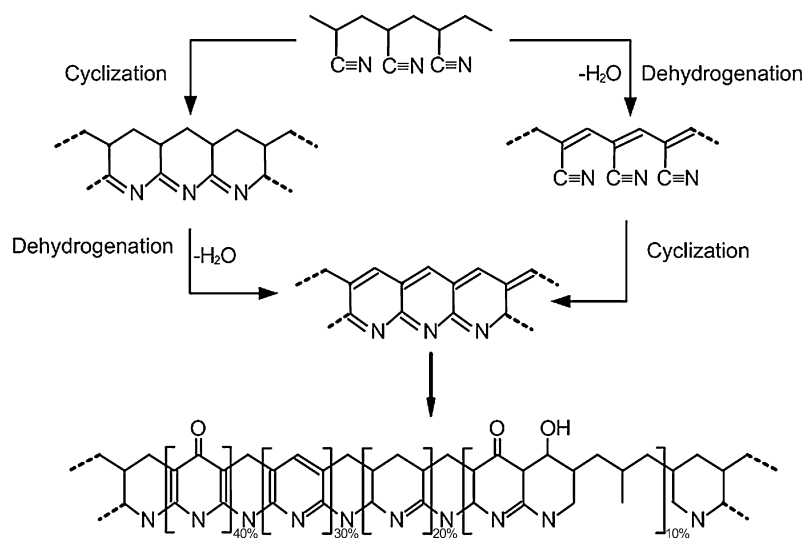


Fig. 3. Proposed chemistry of PAN stabilization [9,40].

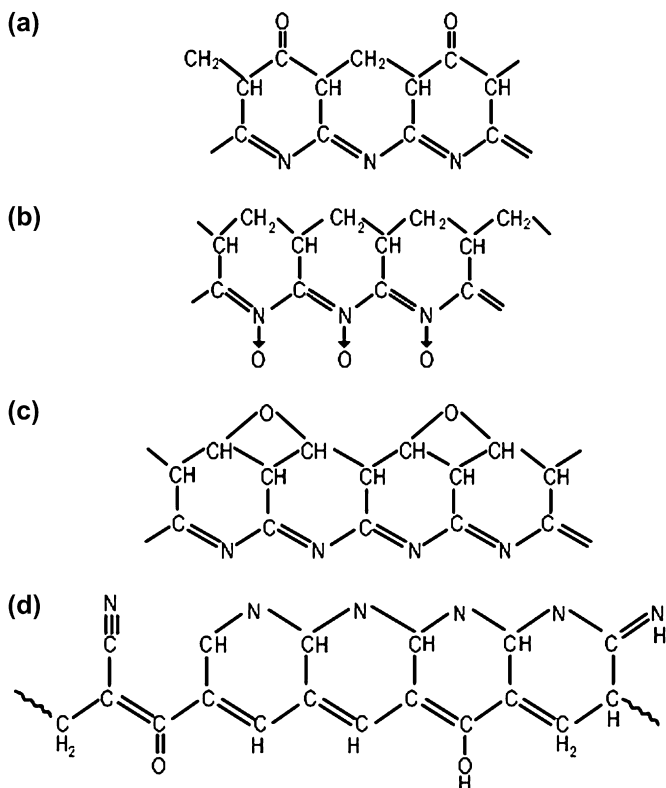


Fig. 5. Proposed structures of oxidized PAN: (a) bridging ether links; (b) carbonyl groups; (c) donation of lone pair electron to oxygen atom; (d) hydroxyl and carbonyl groups [44,45].

Houtz [51] in 1950 from his observation that PAN stabilization led to change in colouration.

During the stabilization process, the PAN structure undergoes cyclization reaction and converts the triple bond structure (e.g. $C\equiv N$) to double bond structure (e.g. $C=N$), resulting in a six-membered cyclic pyridine ring proposed by Houtz [51] as illustrated in Fig. 7 and changes the aliphatic to cyclic structure prior to the formation of ladder polymer. Referring to this figure (Fig. 7), cyclization reactions can proceed in either an inert atmosphere or in the presence of oxygen. In other words, oxygen is not involved in the reaction mechanism of cyclization. When the temperature rises up to $600\text{ }^\circ\text{C}$, the cyclized structure undergoes dehydrogenation and links up in lateral direction, producing a graphite-like

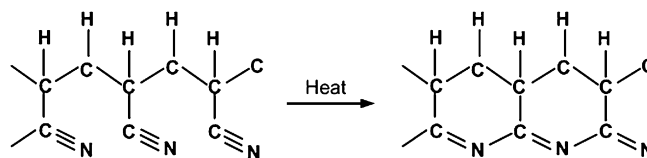


Fig. 7. Fully aromatic cyclized structure proposed by Houtz [51].

layer or ribbon structure (shown in Fig. 8) consisting of three hexagons in the lateral direction and bounded by nitrogen atom [52].

The initiation of the cyclization reaction has been attributed to several sources: (1) impurities such as catalyst fragments, residual polymerization products, inhibitors, etc. [53] (2) the chain end groups; [54] (3) random initiation by hydrogen atoms α to the nitrile; [55] (4) transformation of a nitrile to an azomethine; [56]; (5) the presence of a ketonitrile formed by hydrolysis during polymerization; [28] and (6) hydrolysis of nitriles to acids during polymerization [57]. In addition, due to their reaction, cyclization reactions can proceed in either an inert atmosphere or in the presence of oxygen. In other words, oxygen is not involved in the reaction mechanism of cyclization.

2.4. Miscellaneous types of stabilization process

Although a wide variety of stabilization processes are described, they have several design objectives in common.

1. Runaway reactions from heat must be prevented.
2. Stabilization must be completed throughout the fiber.
3. The shrinkage must be completed throughout the fibers.
4. The reactions are slow and accelerations are helpful.

When the production volume increased specific methods of stabilizing the fiber were patented. The patents deal with three major areas: batch process, continuous process, and acceleration of stabilization reactions. This section provides general example from each of these areas that illustrates common design objectives described above.

2.4.1. Batch process

Three examples of batch processes are shown in Figs. 9–11. The first process blows hot air through a spool precursor loosely wound on a porous core. The air permits heat removal

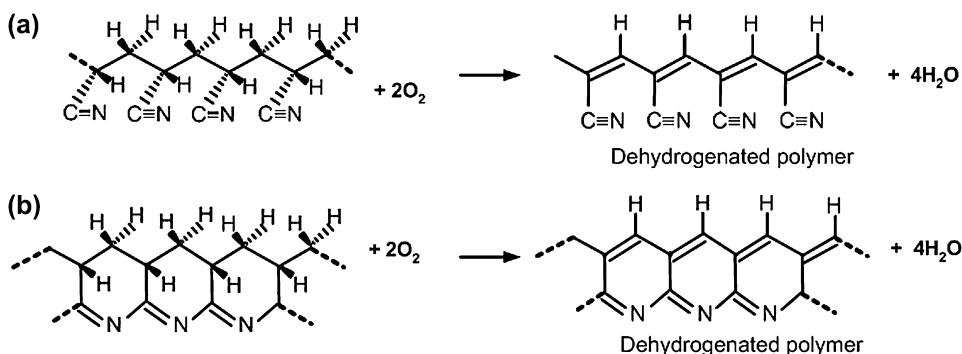


Fig. 6. The dehydrogenation reaction during stabilization process: (a) PAN polymer; (b) cyclized PAN.



Fig. 8. Schematic of graphite ribbon [52].

and provides a source of oxygen. Shrinkage is controlled by the fiber itself as it is wound and spool. However, since the air flow is not uniform and the fibers are in contact with one another, a batch process with a method to move the yarn and improve the uniformity was developed as in Fig. 10. The ends are tied and the rollers turned to minimize the

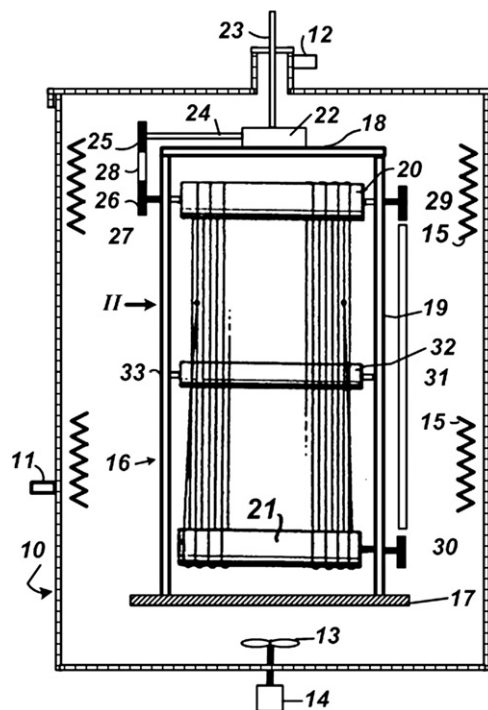


Fig. 10. Moving rack process by atomic energy authority [59].

contact of the yarn with the rollers. And the shrinkage is controlled by adjusting the tension applied to the rack. The final process in Fig. 11 is a step toward continuous process and probably is more expensive to operate than the two processes (Figs. 9 and 10) described before. The initial stages of stabilization are performed continuously in a multiphase oven with the fiber restrained from shrinkage by the oven roller. The more stable final stages are completed in batch oven where the yarn is wrapped into loose skeins. However, the process is limited in its ability to produce since the yarn in contact with the support will differ from that surrounded by air, and the tension is not uniform in the skein.

2.4.2. Continuous process

The continuous processes for stabilizing PAN are all based on the idea of pulling tows through heated boxes. The first sketch in Fig. 12 illustrates the basic heated box with multiple passes. The tow may be oriented horizontally or vertically in the oven and the air in the oven is circulated to control heat and mass transfers.

It also patented by Toho Company [61], where the fiber passes through the oven, turns on a roller, and re-enters the oven. In addition, the heat is controlled by the yarn moving outside the hot oven every few minutes. Meanwhile Courtaulds (Fig. 13) has patented a stabilization oven which contains a number of different temperature zones in a single oven [62]. The yarn is wound on long rollers which pass through a series of baffled oven zones. This concept of multiple zones with a stage temperature is probably used in all commercial processes. An interesting continuous process is shown by the fluidized bed process (Fig. 14) [63]. Here the fibers are

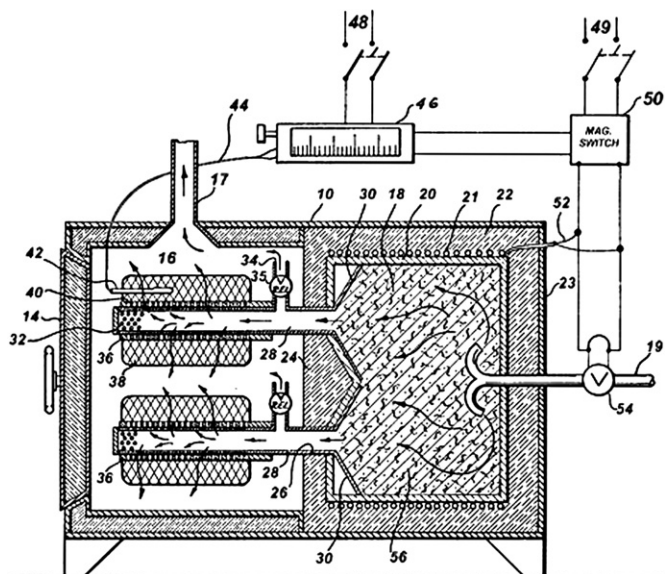


Fig. 9. Batch stabilization of polyacrylonitrile yarn on the tube [58].

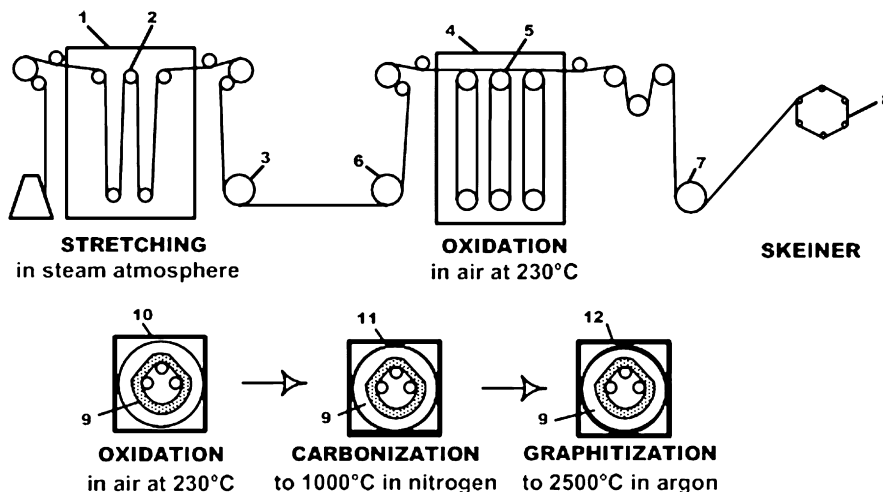


Fig. 11. Semi-batch production of carbon fibers from PAN fiber [60].

passed through a bed of fluidized hollow balls, significantly improving the heat and mass transfer rates. This design could allow the use of higher temperatures and still avoid runaway reaction and should allow more rapid dehydrogenation and oxidation.

2.4.3. Accelerator process

Most accelerators serve as initiators for the cyclization reactions. An example of this is the introduction of acidic groups like itaconic acids which was claimed by the US patent 4,079,122 [64]. This monomer contains two acid groups which provide two initiation sites, leaving fewer uncyclized links for later carbonization. Besides, the US patent 4,397,831 [61] claimed that by passing the fibers through a bath which contains a water-soluble zinc compound and then washes the fiber with the water, could result in Lewis acid served to initiate the cyclization reaction. Other than that, an example for accelerator process by modifying the stabilization gas is given by the US patent 3,954,947 [65]. An atmosphere of oxygen and hydrogen chloride is used, resulting in shorter times for complete stabilization.

3. Carbonization

Carbonization was an aromatic growth and polymerization, in which the fiber would undergo heating process at a high

temperature up to 800–3000 °C, typically to a 95% carbon content [31]. Carbonization at 1000 °C will produce carbon fiber in low modulus type and intermediate modulus or type II carbon fiber will produce at up to 1500 °C [13,16,31,66]. Trinquecoste and group [67], also observed that heating process around 1000 °C produced high tensile strength fiber, and for high modulus fiber, higher temperature treatment is needed. Thus, it would change the PAN structure as illustrated Fig. 15 [68] and Fig. 16 [69].

A few researchers had put in effort to understand the carbonization step especially in continuous model [21]. However, whatever be the technique, the process only occurs in inert atmosphere condition and usually involves heating the polymer in a nitrogen rich environment (Fig. 17) [70]. In addition, tensile and modulus have shown significant increase with carbonization treatment under N₂ [71]. But some researchers proved that argon also can act as inert gas in carbonization process [72–76]. Whereas, carbonizing the stabilized PAN fiber in an atmosphere of HCl vapors could enhance the carbon fiber yield, subsequently decreasing the amount of hydrogen cyanide (HCN) by eliminating nitrogen as ammonia. However,

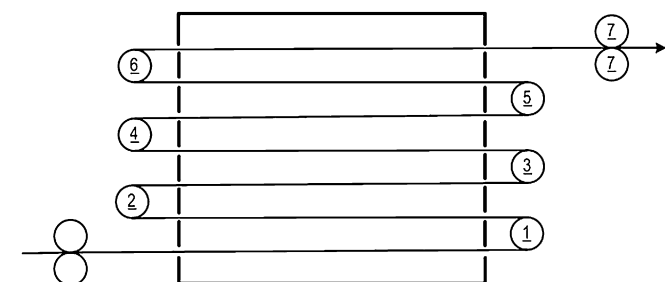


Fig. 12. Continuous stabilization process with roller outside the oven [61].

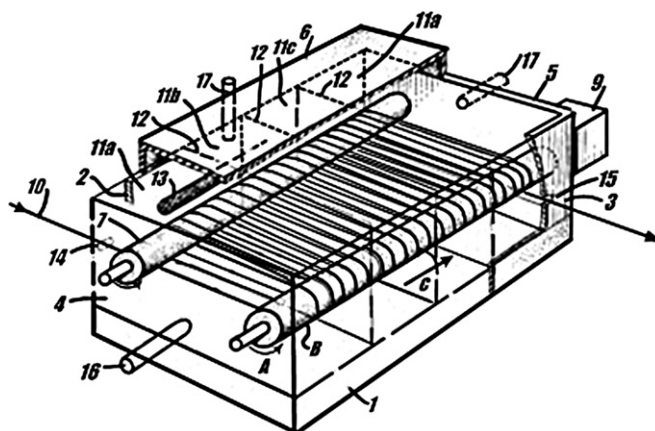


Fig. 13. Courtaulds furnace for oxidation, carbonization and graphitization [62].

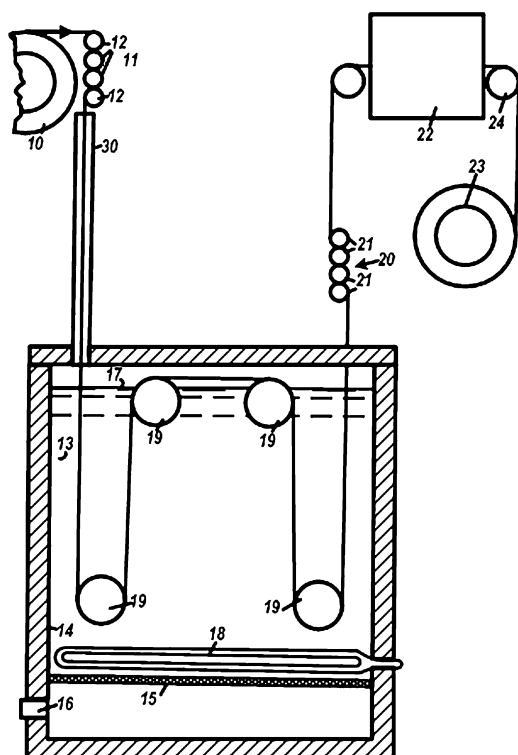


Fig. 14. Rolls-Royce equipment for stabilization of PAN fiber in a fluidized bed [63].

the consumption of argon and HCl was very costly and HCl could make the equipment corrosive [76,77].

In carbonization process, there are two steps wherein, the first step involves in carbonization process and is the thermal pyrolysis up to 600 °C. Low heating rate as low as 5 °C/min was used which could lower the mass transfer because of inability of the structure [35]. In the second stage, high heating rate for high final temperature is needed.

Unlike the first stage, the high heating rate had been used in the second stage because of lesser possibility of damage to the structure due to stability of PAN structure [38]. Thus, the process requires only less than 10 min for the second stage [78]. However, previous study claimed that too high heating rate could cause higher amount of shrinkage [16,35]. Some studies

stated that PAN fiber that stabilized at temperature fewer than 250 °C could not withstand at high heating rate beyond 1700 °C and produced a brittle fiber [38]. Hence, the optimum carbonization was required in order to form better properties of final carbon fiber.

3.1. Stretching during pyrolysis

Stretching during pyrolysis process helps to develop high tensile modulus and improves fiber strength upon subsequent heat treatment. Some study indicated that the strength of the fiber had been restored and could be improved when the high temperatures were accompanied by reasonable degree of stretching [79]. Tsai and Lin [80] and Edie [33] also stated that with the requirement of the stretching in this step, adequate modulus and strength of carbon fiber could be produced.

Other than that stretching could attenuate amount of shrinkage, which was caused by high heating rate [70]. Therefore, if no stretching was applied in the early stage of pyrolysis, then the length shrinkage and the loss of preferred orientation occur and hence deteriorate the mechanical properties of carbon fiber [80].

4. Graphitization

For further improvement on the performance, carbonized fiber must undergo graphitization process. Graphitization is the transformation of carbon structure into graphite structure by heat treatment as well as thermal decomposition at high temperature processing. Actually, the process of production of both carbon fiber and graphite fiber was essentially the same either in carbonization or in graphitization. During graphitization the temperature does not only rise until 1600 °C, but exceeds up to 3000 °C [38,77,81]. In other words, graphitization process was a carbonization process at high heating temperature. At this stage, up to 99% of PAN polymer was converted to carbon structure. Carbon fiber which was produced in this condition was in very high modulus fiber or can be classified as type I carbon fiber.

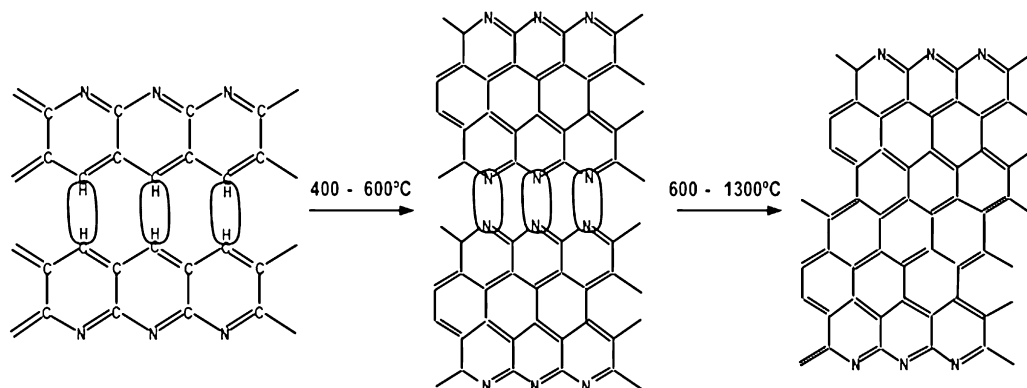


Fig. 15. Structure changes for PAN precursor during carbonization [68].

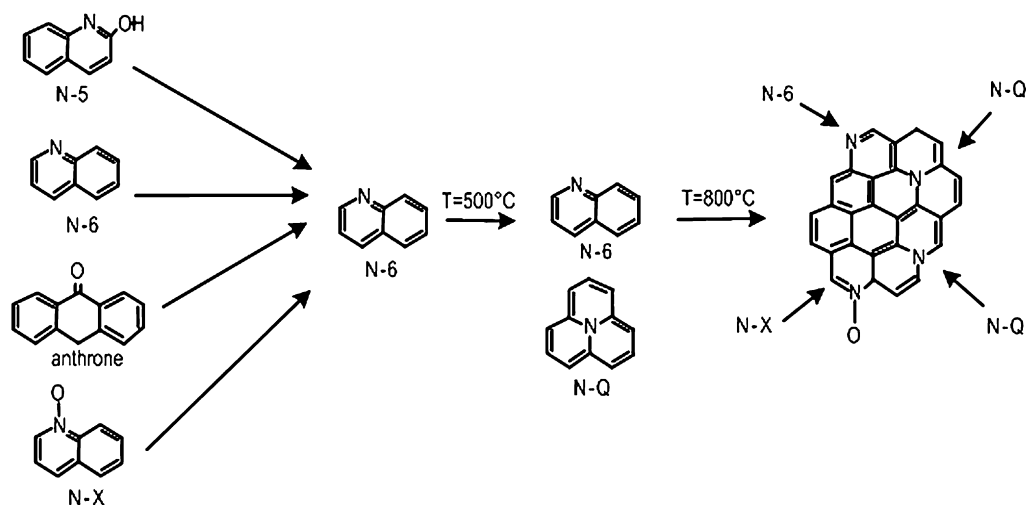


Fig. 16. Sketch of the structural and chemical transformation of the stabilized PAN precursor along with increasing carbonization temperature. N-5, cetopyridine; N-6, pyridine-like N; N-X, pyridine-N-oxide; N-Q, graphitic-like N [69].

5. Functionality gaseous

Generally, carbonized fiber can be found when the temperature reaches 1200 °C and above in inert atmosphere [76]. Through the heating process, the fiber could expel impurities as volatile by-products such as methane (CH₄), hydrogen (H₂), hydrogen cyanide (HCN), water (H₂O), CO₂, NH₃ and various gases [25,33,35,82]. Among that gases, HCN, NH₃ and CO are the toxic compounds that evolved during pyrolysis [83]. But, HCN and NH₃ are the major toxic gases that evolved from decomposition of PAN. Data pertaining to evolution of gases during the carbonization process, from Donnet and Bahl [84], are shown in Fig. 18.

The other factor that promoted excessively volatile component was high stabilization temperature. High stabilization temperature promotes over absorption of oxygen in stabilized fiber and might form excessive –C=O bonds. Usually, the oxygen in these bonds escapes as water vapor [25]. It is known that the decrease of oxygen as water vapor is due to evolution of H₂O in the early stages of carbonization in the range between 300–500 °C. The evolution of H₂O results from the crosslinking condensation reactions between two monomer units of the adjacent ladder polymeric molecular chains which is illustrated in Fig. 19 [85]. When the temperature increased up to 800 °C, hydrogen cyanide and ammonia were the side gases which also evolved and released with water [68]. Watt [86] stated that reaction involving chain termination have

been stated as the reason for the formation of ammonia. This could be either by the formation of ammonia from active chain ends, or by the end-to-end joining of two ladder structure (Fig. 20A). While, the mechanisms for evolution of hydrogen cyanide by the same author are shown in Fig. 20A,B.

Meanwhile, the formation of N₂ has been found to start early at 720 °C [68] and more nitrogen was eliminated from the bulk than from the surface during this heating process [69]. Evolution of nitrogen and hydrogen was explained by Watt [86] with the scheme in Fig. 21. This results in nitrogen atoms substituted in the hexagonal lattice of aromatized carbon, and explains the presence of large amounts of nitrogen in the carbonized fiber. Graphitization at higher temperatures reduces the concentration of residual nitrogen to very small levels. An alternate scheme for dehydrogenation and denitrogenation has been proposed by Zhu et al. [68] and is shown in Fig. 15. In addition, there is also elimination of CH₄, CO₂ and CO that occurs at temperature higher than 800 °C [87].

As a result, the gases were removed until the fiber contains up to 50% carbon content and above [9,88,89]. Sometimes, when the temperature increased up to 1300 °C, the carbonized PAN fiber could achieve 96% carbon content [31]. The increase in the carbon would decrease the nitrogen, hydrogen and oxygen content [25,31,69]. Table 1 shows the percentage of nitrogen and hydrogen which was released from the fiber and the increase of carbon content when the temperature rises. The release of the gases would result in loss in the fiber weight

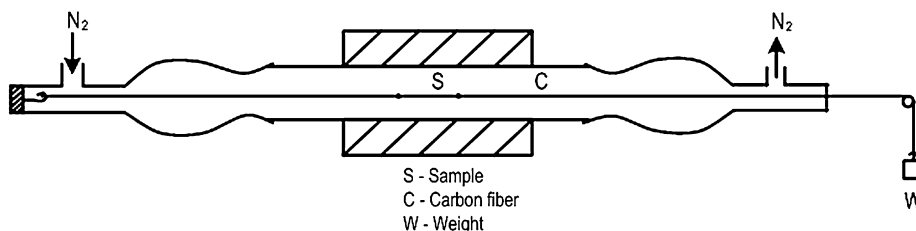


Fig. 17. Schematic diagram of the apparatus used for carbonization [70].

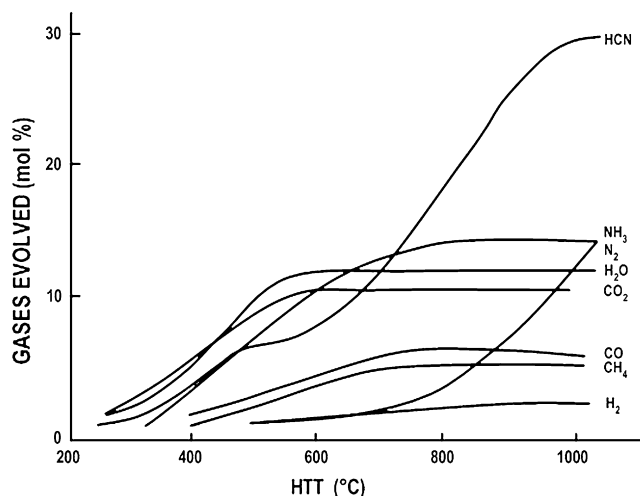


Fig. 18. Evolution of noncarbon elements from PAN fiber during carbonization [84].

within 55–60 wt%, and likely generate pores [33]. Some studies divided the decrease in the weight into two conditions, for about 32% weight loss in the range of 350–800 °C and 13% loss within 900–1000 °C [90]. However, no weight loss was observed beyond 1900 °C, and the fiber contains only carbon [91].

Much of the research work has been done either to improve mechanical properties or to decrease the manufacturing cost of carbon fiber [4,35,92]. The manufacturing of carbon fiber is not an easy task due to their strict procedure. The fiber also tends to brittle without proper control on optimization process. Therefore, a comprehensive study should be done to find the optimum condition for the production of carbon fiber with excellent performance that used in advanced materials and becoming worldwide application.

6. Effect of heating treatment on PAN-based carbon fiber properties

The characteristics of PAN-based carbon fiber could be measured through infrared spectra. The infrared spectrum would identify whether the PAN fiber was stabilized and carbonized or not. Sometimes the characteristic was measured by physical properties as well as the diameter and the density of the fiber. There was a relationship between diameter, density

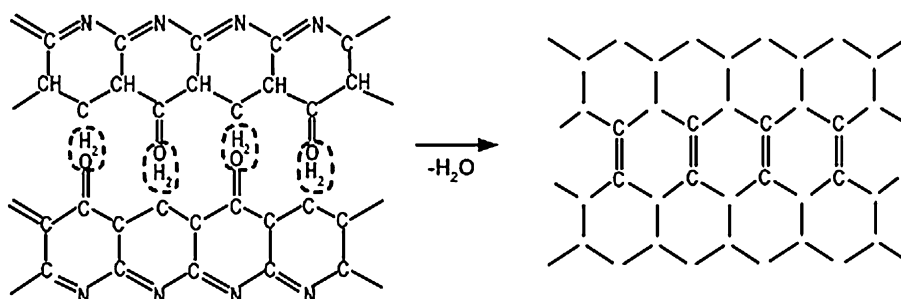


Fig. 19. The crosslinking condensation reactions between two monomer units of the adjacent ladder polymeric chains [85].

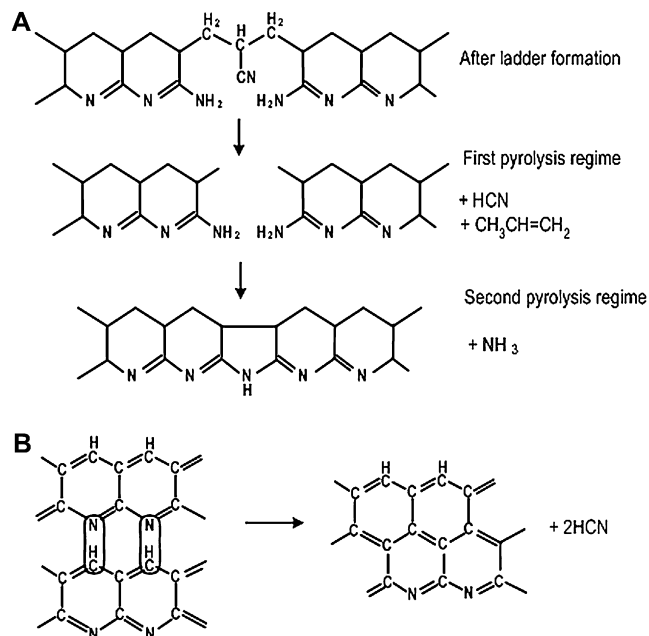


Fig. 20. (A) Elimination of NH_3 and HCN at low temperatures; (B) high-temperature elimination of HCN [86].

and performance of carbon fiber. Mittal et al. [38] observed that generally when the diameter decreased, the density would be increased. In general, reducing the PAN fiber diameter and increasing fiber density could make the fiber denser and hence improved the performance of carbon fiber. The improvement could be done by introducing proper treatment especially heat treatment.

6.1. Infrared (IR) characteristics

Infrared (IR) spectra can be used to analyze the chemical structure that exists in the fiber. According to IR analyzes, PAN fiber showed prominent peaks at 2940 cm^{-1} ($-\text{CH}$ stretch), 2240 cm^{-1} ($\text{C}\equiv\text{N}$ stretch) and 1452 cm^{-1} ($-\text{CH}_2$ bend) and for SAF with 1% IA and 6% MA, the carbonyl stretch of comonomer units appeared at 1730 cm^{-1} [23].

Conley and Beron [93] stated that two dominant peaks, which are at 2940 cm^{-1} and 2240 cm^{-1} start decreasing at $180\text{ }^\circ\text{C}$ due to the formation of cyclization reaction. However, Coleman and coworkers [94–99] suggested that the

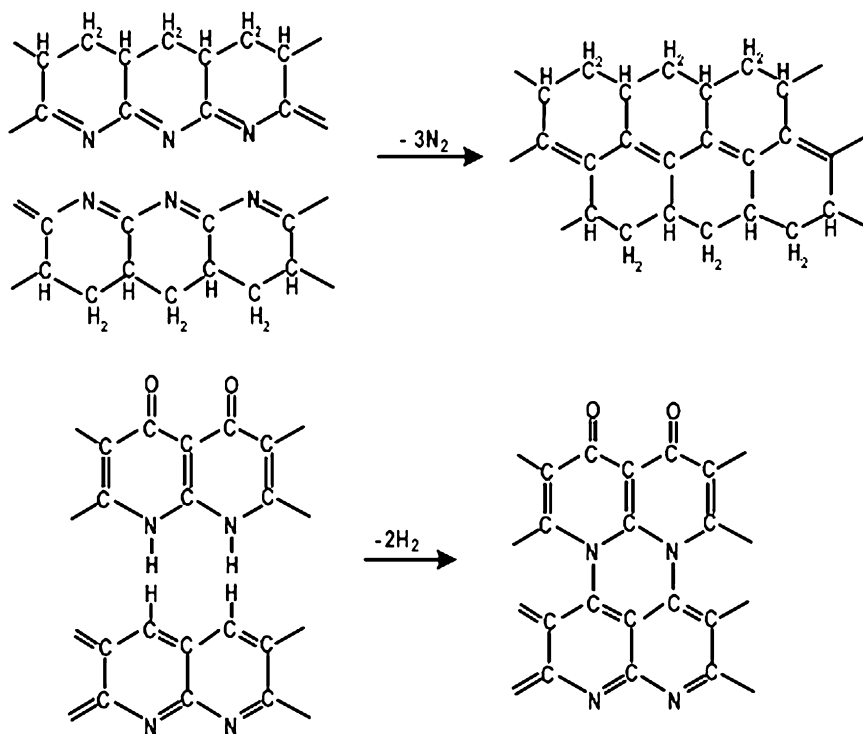


Fig. 21. Elimination of N_2 and H_2 at high temperature [86].

disappearance of 2240 cm^{-1} band for the nitrile began as early as 160°C under vacuum. Setnescu et al. [27] observed, through pyrolysis process, that two peaks almost completely disappeared and new peaks appeared around 800 cm^{-1} and 1600 cm^{-1} . The change in peaks are due to the formation of $C=C$, $C=N$ and $=C-H$ and results in the formation of carbon fiber structure.

and produced small fiber diameter. Sometimes a diameter with ten times lower than human hair could be produced [16]. The significant reduction in diameter has been observed within the carbonization temperature (below 1000°C) [38]. Similar trend of the reduction of fiber diameter has been found by Liu et al. [21]. In other words, the diameter diminished throughout the carbonization treatment.

6.2. Diameter

Large diameter is one of the limitations of fiber strength. As mentioned before, to give uniformity in heat treatment, fibers must have a small diameter. Chen and Harrison [16], stated that small diameter can reduce any gradient temperature across the fiber to form uniformity of heat treatment.

Commercial PAN fiber like Dralon T (DT) and Special Acrylic Fiber (SAF) have diameter in the range of $8\text{--}20\text{ }\mu\text{m}$ [23]. As stated before, plasticizer is applied in post-spinning modification to reduce fiber diameter prior to heat treatment. When heat treatment has been applied as well as the rise in the temperature, the diameter of the fiber would shrink again

6.3. Density

Various studies indicated that a significant change in the fiber density occurred below carbonization temperature [31,81,100]. Within the carbonization temperature ($300\text{--}1200^\circ\text{C}$), the changes in the density of the fibers take place up to 800°C [38]. Sometimes, it could rapidly change up to 1000°C [31]. The density could be changed due to the compaction of the structure taking place during the early stages of carbonization. It is also due to the presence of the noncarbon elements in the fiber and the ladder polymer structures interconnecting with one another [100].

However, the density increase was followed by a sharp drop at 1000°C which is due to the conversion of open pores to closed pores [31]. As a consequence, the air would be trapped inside the fibers and hence results in low density which could limit the tensile strength of the final carbon fiber [25]. However, Ozbek and Isaac [79] and Sauder et al. [101] observed that heating temperature (HTT), which increases up to 3000°C , can eliminate the effect of open and closed pores. This is because, in this region high heating rate and high temperature were used which made the vibrations of molecules

Table 1
Chemical composition of some pyrolyzed PAN samples found by elemental analysis [27]

Pyrolysis temperature ($^\circ\text{C}$)	Element content		
	Carbon (%)	Nitrogen (%)	Hydrogen (%)
Initial	66.33	26.00	5.47
600	68.51	11.93	3.69
900	75.46	6.28	1.46

faster. So, the air in closed pores will be freed and thus reduces the number of closed pores.

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References

- [1] Schwartz M. Encyclopedia of materials, parts, and finishes. 2nd ed. Boca Raton, Florida: CRC Press; 2002.
- [2] Cato Anthony D, Edie DD. Flow behavior of mesophase pitch. Carbon 2003;41(7):1411–7.
- [3] Bahl OP, Manocha LM. Characterization of oxidized PAN fibers. Carbon 1974;12(4):417–23.
- [4] Bahl OP, Mathur RB. Effect of load on the mechanical properties of carbon fibres from PAN precursor. Fiber Sci Technol 1979;12(1):31–7.
- [5] Donnet JB, Bansal RC. Carbon fibers. New York: Marcel Dekker Inc.; 1984.
- [6] Wangxi Z, Jie L, Gang W. Evolution of structure and properties of PAN precursors during their conversion to carbon fibers. Carbon 2003;41(14):2805–12.
- [7] Sánchez-Soto PJ, Avilés MA, del Río JC, Ginés JM, Pascual J, Pérez-Rodríguez JL. Thermal study of the effect of several solvents on polymerization of acrylonitrile and their subsequent pyrolysis. J Anal Appl Pyrolysis 2001;58–59:155–72.
- [8] Chung DDL. Handbook of applied materials science applications—engineering materials in structural, electronics, thermal, and other industries. London: CRC Press; 2001.
- [9] Wiles KB. Determination of reactivity ratios for acrylonitrile/methyl acrylate radical copolymerization via nonlinear methodologies using real time FTIR. MSc thesis, Faculty of the Virginia Polytechnic Institute and State University: Blacksburg, Virginia; 2002.
- [10] Bahl OP, Mathur RB, Kundra KD. Structure of PAN fibers and its relationship with resulting carbon fiber properties. Fiber Sci Technol 1981;15(2):147–51.
- [11] Yang MC, Yu DC. Influence of precursor structure on the properties of polyacrylonitrile-based activated carbon hollow fiber. Appl Polym Sci 1996;59:1725–31.
- [12] Donnet JB, Bansal RC. Carbon fibers. 2nd ed. New York: Marcel Dekker Inc.; 1990.
- [13] Mittal J, Mathur RB, Bahl OP. Post spinning modification of PAN fibers. Carbon 1997;35(12):1713–22.
- [14] Pamula E, Rouxhet GP. Bulk and surface chemical functionalities of type III PAN-based carbon fibers. Carbon 2003;41(10):1905–15.
- [15] Fitzer E. PAN based carbon – present state and trend of the technology from the viewpoint of possibilities and limit to influence to control the fiber properties by the process parameter. Carbon 1989;27(5):621–45.
- [16] Chen JC, Harrison IR. Modification of polyacrylonitrile (PAN) carbon fiber precursor via post-spinning plasticization and stretching in dimethylformamide (DMF). Carbon 2002;40(1):25–45.
- [17] Ogawa H. Architectural application of carbon fibers development of new carbon fiber reinforced glulam. Carbon 2000;38(2):211–26.
- [18] Traceski TF. Assessing industrial capabilities for carbon fiber. USA: Acquisition and Technology; 1999.
- [19] Tullo AH. Chem Eng News 2000;78:11–5.
- [20] Bhanu VA, Rangarajan P, Wiles K, Bortner M, Sankarpandian M, Godshall D, et al. Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors. Polymer 2002;43(18):4841–50.
- [21] Liu J, Wang PH, Li RY. Continuous carbonization of polyacrylonitrile-based oxidized fibers: aspects on mechanical properties and morphological structure. Appl Polym Sci 1994;52(7):945–50.
- [22] Bashir Z. A critical review of the stabilization of polyacrylonitrile. Carbon 1991;29(8):1081–90.
- [23] Dalton S, Heatley F, Budd PM. Thermal stabilization of polyacrylonitrile fibers. Polymer 1999;40(20):5531–43.
- [24] Clingerman ML. Development and modelling of electrically conductive composite materials. PhD thesis, Michigan Technological University: USA; 2001.
- [25] Ko TK. Influence of continuous stabilization on the physical properties and microstructure of PAN-based carbon fibers. Appl Polym Sci 1991;42(7):1949–57.
- [26] David LIB, Ismail AF. Influence of the thermostabilization process and soak time during pyrolysis process on the polyacrylonitrile carbon membranes for O₂/N₂ separation. J Membr Sci 2002;213(1–2):285–91.
- [27] Setnescu R, Jipa S, Setnescu T, Kappel W, Kobayashi S, Osawa Z. IR and X-ray characterization of the ferromagnetic phase of pyrolysed polyacrylonitrile. Carbon 1999;37(1):1–6.
- [28] Friedlander HF, Peebles Jr LH, Brandrup J, Kirby JR. On the chromophore of polyacrylonitrile VI. Mechanism of color formation in polyacrylonitrile. Macromolecules 1968;1(1):79–86.
- [29] Burlant WJ, Parsons JL. Pyrolysis of polyacrylonitrile. J Polym Sci 1956;22(101):249–56.
- [30] Paiva MC, Kotasthane P, Edie DD, Ogale AA. UV stabilization route for melt-processible PAN-based carbon fibers. Carbon 2003;41(7):1399–409.
- [31] Ko TH. The Influence of pyrolysis on physical properties and microstructure of modified PAN fibers during carbonization. Appl Polym Sci 1991;43(3):589–600.
- [32] Martin SC, Liggat JJ, Snape CE. In situ NMR investigation into the thermal degradation and stabilization of PAN. Polym Degrad Stab 2001;74(3):407–12.
- [33] Edie DD. The effect of processing on the structure and properties of carbon fiber. Carbon 1998;36(4):345–62.
- [34] Ogawa H, Saito K. Oxidation behavior of polyacrylonitrile fibers evaluated by new stabilization index. Carbon 1995;33(6):783–8.
- [35] Fitzer E, Frohs W, Heine M. Optimization of stabilization and carbonization of PAN fibers and structural characterization of the resulting carbon fibers. Carbon 1986;24(4):387–95.
- [36] Gupta A, Harrison IR. New aspect in the oxidative stabilization of PAN based carbon fibers II. Carbon 1997;35(6):809–18.
- [37] Gupta A, Harrison IR. New aspects in the oxidative stabilization of PAN-based carbon fibers. Carbon 1996;34(11):1427–45.
- [38] Mittal J, Mathur RB, Bahl OP. Single step carbonization and graphitization of highly stabilized PAN fibers. Carbon 1997;35(8):1196–7.
- [39] Mathur RB, Bahl OP, Mittal J. A new approach to thermal stabilization of PAN fibers. Carbon 1992;30(4):657–63.
- [40] Bansal RC, Donnet JB, Stoeckli F. Active carbon. New York: Marcel Dekker Inc.; 1988.
- [41] Beltz LA, Gustafson RR. Cyclization kinetics of polyacrylonitrile. Carbon 1996;34(5):561–6.
- [42] Rangarajan P, Bhanu VA, Godshall D, Wikels GL, McGrath JE, Baird DG. Dynamic oscillatory shear properties of potentially melt processable high acrylonitrile terpolymers. Polymer 2002;43(9):2699–709.
- [43] Fitzer E, Muller DJ. The Influence of oxygen on the chemical reaction during stabilization of PAN as carbon fiber precursor. Carbon 1975;13(1):63–9.
- [44] Riggs DM, Shuford RJ, Lewis RW. Handbook of composites. In: Lubin G, editor. New York: Van Nostrand Reinhold; 1987.
- [45] Donnet JB, Wang TK, Peng JCM, Rebouillat S. Carbon fiber. 3rd ed. Marcel Dekker Inc.; 1998.
- [46] Peebles Jr LH, Peyser P, Snow W, Peters WC. On the exotherm of polyacrylonitrile: pyrolysis of the homopolymer under inert conditions. Carbon 1990;28(5):707–15.
- [47] Grassie N, Hay JN, McNeill IC. Thermal coloration and insolubilization in polyacrylonitrile. J Polym Sci 1962;56(163):189–202.
- [48] Takata T, Hiroi I, Taniyama M. Coloration in acrylonitrile polymers. J Polym Sci Part A Polym Chem 1964;2(4):1567–85.
- [49] Brandrup J, Peebles Jr LH. On the chromophore of polyacrylonitrile. IV. Thermal oxidation of polyacrylonitrile and other nitrile-containing compounds. Macromolecules 1968;1(1):64–72.

- [50] Grassie N, McGuchan R. Pyrolysis of polyacrylonitrile and related polymers. III. Thermal analysis of preheated polymers. *Eur Polym J* 1971;7(10):1357–71.
- [51] Houtz RC. Orlon acrylic fiber: chemistry and properties. *Text Res J* 1950;20(11):786–801.
- [52] Fourduex A, Perret R, Ruland W. Carbon fibers – their composites and applications. London: The Plastic Institute; 1971.
- [53] Grassie N, McGuchan R. Pyrolysis of polyacrylonitrile and related polymers – I. Thermal analysis of polyacrylonitrile. *Eur Polym J* 1970;6(9):1277–91.
- [54] Thompson EV. The thermal behavior of acrylonitrile polymers. I. On the decomposition of polyacrylonitrile between 250 and 325 °C. *Polym Lett* 1966;4(5):361–6.
- [55] Grassie N, McGuchan R. Pyrolysis of polyacrylonitrile and related polymers – VI. Acrylonitrile copolymers containing carboxylic acid and amide structures. *Eur Polym J* 1972;8(2):257–69.
- [56] Shurz J. Discoloration effects in acrylonitrile polymers. *J Polym Sci* 1958;28(117):438–9.
- [57] Peebles Jr LH, Thompson Jr RB, Kirby JR, Gibson ME. Basic dyeability and acid content of high-conversion polyacrylonitrile. *J Appl Polym Sci* 1972;16(12):3341–51.
- [58] Barnett I, Somerville NJ. Thermal modification of acrylonitrile yarns. US patent 2,913,802; 1959.
- [59] Longstaff B. Production of carbonized fibers. US patent 3,547,420; 1970.
- [60] Prescott R, Jonesboro, Weaver OI. Process for the manufacture of continuous high modulus carbon yarns and monofilaments. US patent 3,533,743; 1970.
- [61] Saito K, Ogawa H. Productions of carbon fiber from acrylonitrile based fibers. US patent 4,397,831; 1983.
- [62] Townsend BA, Rugby continuous carbon filament production. US patent 3,567,380; 1971.
- [63] Wirksworth IW, Johnson JW, Allestree Derby. Method of manufacturing carbon fibers. US patent 3,615,212; 1971.
- [64] McLouglin VCR, Moreton R, Watt W. Preparation of carbon fibers. US patent 4,079,122; 1978.
- [65] Didchenko R, Amata CD. Rapid stabilization of polyacrylonitrile fibers prior to carbonization. US patent 3,954,947, 1976.
- [66] Donnet JB, Bansal RC, Bahl OP. Encyclopedia of physical science and technology, vol. 2. New York: Academic Press; 1992.
- [67] Trinquocoste M, Carlier JL, Derré A, Delhaes P, Chadeyron P. High temperature thermal and mechanical properties of high tensile carbon single filaments. *Carbon* 1996;34(7):923–9.
- [68] Zhu D, Xu C, Nakura N, Matsuo M. Study of carbon films from PAN/VGCF composites by gelation/crystallization from solution. *Carbon* 2002;40(3):363–73.
- [69] Laffont L, Monthieux M, Serin V, Mathur RB, Guimon C, Guimon MF. An EELS study of the structural and chemical transformation of PAN polymer to solid carbon. *Carbon* 2004;42(12–13):2485–94.
- [70] Wu Z, Pan D, Fan X, Qian B. Thermal shrinkage behavior of preoxidized polyacrylonitrile fibers during carbonization. *Appl Polym Sci* 1987;33(8):2877–84.
- [71] Lee JK, Shim HJ, Lim JC, Choi GJ, Kim YD, Min BG, et al. Influence of tension during oxidative stabilization on SO₂ adsorption characteristics of polyacrylonitrile (PAN) based activated carbon fibers. *Carbon* 1997;35(6):837–43.
- [72] Ko TH. Raman spectrum of modified PAN-based carbon fibers during graphitization. *Appl Polym Sci* 1996;59(4):577–80.
- [73] Wang PH. Conversion of polyacrylonitrile fibers to activated carbon fibers: effect of preoxidation extent. *Appl Polym Sci* 1996;62(10):1771–3.
- [74] Lee JK, An KW, Ju JB, Cho BW, Cho WI, Park D, et al. Electrochemical properties of PAN-based carbon fibers as anodes for rechargeable lithium ion batteries. *Carbon* 2001;39(9):1299–305.
- [75] Sung MG, Sassa K, Ogawa H, Tanimoto Y, Asai S. Strengthening of carbon fibers by imposition of a high magnetic field in a carbonization process. *Mater Trans* 2001;43(8):2087–91.
- [76] Chand S. Carbon fiber for composites. *Mater Sci* 2000;35(6):1303–13.
- [77] Kaburagi M, Bin Y, Zhu D, Xu C, Matsuo M. Small angle X-ray scattering from voids within fibers during the stabilization and carbonization stages. *Carbon* 2003;41(5):925–6.
- [78] McCabe. Pretreatment of PAN fiber. US patent 4,662,336; 1987.
- [79] Ozbek S, Isaac DH. Strain-induced density changes in PAN-based carbon fibers. *Carbon* 2000;38(14):2007–16.
- [80] Tsai JS, Lin CH. The effect of the side chain of acrylate comonomers on the orientation, pore size distribution, and properties of polyacrylonitrile precursor and resulting carbon fiber. *Appl Polym Sci* 1991;42(11):3039–44.
- [81] Mittal J, Mathur RB, Bahl OP, Inagaki M. Post spinning treatment of PAN fibers using succinic acid to produce high performance carbon fibers. *Carbon* 1998;36(7–8):893–7.
- [82] Riggs DM, Shuford RJ, Lewis RW. Graphite fiber and composites. In: Lubin G, editor. Handbook of composites. New York: Van Nostrand Reinhold; 1982. p. 196–271.
- [83] Nielsen M, Jurasek P, Hayashi J, Furimsky E. Formation of toxic gases during pyrolysis of polyacrylonitrile and nylons. *Anal Appl Pyrolysis* 1995;34(1):43–51.
- [84] Donnet JB, Bahl OP. Encyclopedia of physical science and technology, vol 2. New York: Academic Press Inc.; 1987.
- [85] Manocha LM, Bahl OP. Role of oxygen during thermal stabilization of PAN fibres. *Fiber Sci Technol* 1980;13(3):199–212.
- [86] Watt W. In: Watt W, Perov BB, editors. Chemistry and physics of conversion of PAN fibers into high-modulus carbon fiber. *Strong fiber*, vol. 1. Netherlands: Elsevier Science Publishers; 1985. p. 327.
- [87] Fitzer E, Heine M. Proceeding 16th biennial conference on carbon fibers. San Diego, CA, USA: American Carbon Society; 1983. p. 501–3.
- [88] Watt W, Green J. Proceeding of the international conference on carbon fibers, their composites and applications. London: Plastics Inst; 1971. p. 23–26.
- [89] Watt W, Johnson DJ, Parker E. Proceeding of the second conference on carbon fibers. London: Plastic Inst; 1974. p. 3–7.
- [90] Mittal J, Konno H, Inagaki M, Bahl OP. Denitrogenation behavior and tensile strength increase during carbonization of stabilized PAN fibers. *Carbon* 1998;36(9):1327–30.
- [91] Zhu Z, Liu Z, Gu Y. Formation of N₂ during carbonization of polyacrylonitrile using iron catalyst. *Fuel* 1997;76(2):155–63.
- [92] Jain MK, Abhiraman AS. Conversion of acrylonitrile-based precursor fibers to carbon fibers. *J Mater Sci* 1987;22(1):278–300.
- [93] Conley RT, Beron JE. Examination of the oxidative degradation of polyacrylonitrile using infrared spectroscopy. *Appl Polym Sci* 1963;7(5):1757–73.
- [94] Coleman MM, Petcavich RJ. Fourier transform infrared studies on the thermal degradation of polyacrylonitrile. *Polym Sci Polym Phys* 1978;16(5):821–32.
- [95] Coleman MM, Sivy GT. Fourier transform IR studies of the degradation of polyacrylonitrile copolymers – I: introduction and comparative rates of the degradation of three copolymers below 200 °C and under reduced pressure. *Carbon* 1981;19(2):123–6.
- [96] Coleman MM, Sivy GT, Painter PC, Snyder RW, Gordon III B. Studies of the degradation of acrylonitrile/acrylamide copolymers as a function of composition and temperature. *Carbon* 1983;21(3):255–67.
- [97] Petcavich RJ, Painter PC, Coleman MM. Fourier-transform infrared studies on the thermal degradation of poly- α -deuteroacrylonitrile under reduced pressure. *Polym Sci Polym Phys* 1979;17(1):165–8.
- [98] Sivy GT, Gordon III B, Coleman MM. Studies of the degradation of copolymers of acrylonitrile and acrylamide in air at 200 °C. Speculations on the role of the preoxidation step in carbon fiber formation. *Carbon* 1983;21(6):563–8.
- [99] Sivy GT, Coleman MM. Fourier transform IR studies of the degradation of polyacrylonitrile copolymers – II: acrylonitrile/methacrylic acid copolymers. *Carbon* 1981;19(2):127–31.
- [100] Ko TH, Huang LC. The influence of cobaltous chloride modification on physical properties and microstructure of modified PAN fiber during carbonization. *Appl Polym Sci* 1998;70(12):2409–15.
- [101] Sauder C, Lamont J, Pailer R. Thermomechanical properties of carbon fibers at high temperature (up to 2000 °C). *Compos Sci Technol* 2001;62(4):499–504.