Review on the Precursor Preparation and Carbon Fiber Manufacturing

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Abstract. Benefiting from policy promotion and rapid industrial development, the integration of Chinese carbon fiber companies has sprung up, accounting for nearly 70% of the world's total, and overall production capacity has ranked third in the world. This article aims at doing the research on the precursor preparation and carbon fiber manufacturing.

1. Introduction
Carbon fiber reinforced polymer is an advanced thermoplastic composite that is made with carbon fiber and polymer matrix. Carbon fiber provided the required strength and stiffness in the composite, and the polymer matrix acted as a cohesive matrix that holds fibers together. CFRP is outstanding for its high strength, low weight, corrosion resistance, and fatigue resistance properties. In this article, carbon fiber’s development and its manufacturing will be discussed.

2. Carbon fiber
2.1. The first introduction of carbon fiber filament
The first introduction of carbon fiber filament is attributed to Thomas Edison 1879 during his work on incandescent light bulb[1]. At 1960s, Dr. Akio shindo, at Agency of industrial Science and Technology developed a carbon fiber composites based on polyacrylonitrile(PAN). This kind of production method is considered more cost-effective because only 55% of carbon were in such composites. Since late 1970s, different kinds of CFRP were introduced to the market according to their performance such as UHM, HM, IM, HT, and SHT. These CFRP are usually characterized by their weight, density, modulus, fatigue strength, corrosion resistance, thermal expansion, electrical conductivity, etc[2]. Applications are also diverse because of their performance. Commonly CFRP with high strength to weight ratio and stiffness are used in aerospace, superstructure ships, automobile, civil engineering, and technical applications varied by customers[3].

When Thomas Edison invented the first incandescent light bulb, the strip of material or filament in the bulb was considered the first commercial carbon fiber. Unlike petroleum-based carbon fiber we used today, when creating the early filaments, Edison cut the cotton breads or bamboo silver to the proper size and heated them to high temperature. Carbonization took place and filaments became an all-carbon fiber with the same exact shape[4]. Such process method is known as “pyrolysis”, we still use the method to convert waste such as plastic and biomass waste into energy and other valuable products[5]. Although the resulting carbonized filaments have considerable electrical conductivity and heat resistance for incandescence, it lacked the tensile strength as today’s CFRP.
In 1958, Roger Bacon demonstrated the first high performance carbon fiber. Bacon’s early research topic was to find the triple point of carbon. During his research, he accidently found out that the vaporized carbon in a carbon arc furnace would directly transform into solid state when he reduced the pressure force on those carbon. The solid carbon developed by Bacon had width less than human hair but length up to one inch. Such carbon fibers produced by Bacon had a tensile strength of 20 GPa and a Young’s modulus of 700 GPa[6].

2.2. Reinforcing fibers
Since the 1950s, many varieties of reinforcing fibers have been developed. In 1960, Richard Millington developed a manufacturing process while using rayon as a precursor[7].

The basic material he used was rayon fabrics, roving or yarn. Carbon fabrics were produced while cutting these roving and yarns into short length. This non-thermoplastic cellulosic fiber is able to decompose prior to melting when it is under thermal stress.

The first step of his manufacturing process is to sour the fiber by washing with a powerful detergent in heated water. The fiber has to be clean of impurities and finish. After rinsing and drying step, the fibers are exposed to progressively higher temperatures (up to 1000℉). According to Millington, the highest temperature used in progressively heating is below the extreme temperatures that can transfer these fibers to compete carbon form. After heating by elevated temperature, these fibers were converted to carbon fibers. Thereafter, Millington used a higher flash temperature (approximately 2000℉) for further heating steps to improve the thermal characteristics of the product. Finally, the product is cooled to 300℉ under oxidizing conditions. This carbon fiber had sufficient tensile strength around 0.4 Gpa and used as a reinforcement carbon fiber for high temperature resistance application[8]. The rayon-based precursor is not suitable for industrial products. One of the main reasons is that the tensile strength achieved by rayon precursor is poor.

Another reason is the poor yield. Yield of the fiber is corresponds to carbon atom production. Each Cellulose ring unit could produce five carbon atoms. Low carbon content of cellulose determined its poor conversion rate. When compared to PAN, the converting efficiency of cellulose-based precursor is only 10%-30%, compared with 40% to 50% in PAN-based carbon fiber. In addition, 50%-60% weight of the initial precursor lost during the stabilization process. And the hot stretching graphitization process usually required modulus with 620 GPa and tensile strength of 3.1 Gpa to obtain the fibers. As a result, rayon is not an economical choice for mass production industry[14].

2.3. Polyacrylonitrile (PAN) precursor fibers
Polyacrylonitrile (PAN) precursor fibers were firstly produced by DuPont in 110s[9]. At 1960s, Dr. Akio shindo, at Agency of industrial Science and Technology firstly made PAN into carbon fibers. Such technique was licensed to Toray industries in 1970, which is the largest global carbon fiber manufacturer today[12]. Currently, 90% world carbon fiber production relied on PAN precursor to produce carbon fibers. When compared to other precursor polymers such as rayon and pitch, higher tensile strength was usually expected in PAN. PAN is known as the best precursor for high tensile strength carbon fiber production. The behavior of PAN precursor fiber is largely dependent on its structure, which is well ordered laterally in two dimensions with little or no order longitudinally[14].

The PAN-based carbon fiber consisted three material types made of glass, polyaramids, and mainly carbon[10]. In the beginning, PAN co-polymer will be applied to form fibers during the spinning process, in which the different process parameters in spinning process such as the decomposition of the dope, and the temperature and the concentration of the coagulation bath will control the quality of the final fibers. Atomic structure and performance of PAN will be influenced under different spinning condition and composition. Common spinning solution with solvent such as DMSO, DMF, and DMAc is required in such technique since PAN decomposes before melting, which serves to protect formation of fibers.

The concentration of applied dope solution is around 15-25 wt%, which secure the formation of fibers in high mechanical strength. Wet spinning is the most commonly used spinning technology in
industrial production. Other available spinning methods such as melt, dry, and electrospinning are used as appropriate according to material, which usually produce PAN-based carbon fibers with voids and surface defects [11]. Wet spun PAN fiber is outstanding as a precursor for carbon fiber because the its co-polymer will promote carbonation. The further treatment on the fibers including stretching, stabilization, carbonation, and graphitization. After all these steps, the prepared fiber is ready for further application such as prepregs. In order to save manufacturing cost, solvent-water mixture would be separated to water and solvent in the recovery area.

2.4. Pitch-based carbon fiber
Pitch is commonly distilled from carbon-based material such as plants, crude oil, and coal. When compared to PAN precursor, pitch produces the carbon fiber with higher modulus but low strength, which has a sheet structure with easier formation and propagation of cracks[13]. However, pitch-based carbon fiber is well-known for its high yield and occupy 10% carbon fiber production in the World. In order to achieve high average tensile strength, it has to be converted into a mesophase pitch (MP), in which the pitch was stretched at high temperature[14].

However, the flow characteristics of MP make it really hard to be melt down. In industrial production, different solvents will be added to ensure the pitch is more spinnable at elevated temperature[15]. Solvated MP from ConoPhillips Co, USA was employed in the following manufacturing system. The following picture is a schematic diagram of a meltdown fiber spinning equipment. The following spinning system contained a pitch feeding device, extruder, vacuum vent, ballast pump, spinning pump, filter, spinneret head, fiber collector, air flow jet regulator, and temperature and pressure, and vacuum control system, etc. In such process, the pitch-based carbon fiber was prepared by meltdown spinning of solvated MP, in which includes drying, oxidization, and carbonization[16].

![Diagram of melting fiber spinning equipment](attachment:image.png)

Figure 1: 1-pitch feeding; 2-extruder; 3-exhaust vent; 4-ballast pump; 5- spinning pump; 6-filter; 7-spinneret head; 8-primary air stream; 9-secondary air stream; 10-diffuser; 11-air exhaust; 12-spun fiber web; 13-moving belt collector; 14-stabilization oven; 15-carbonization furnace; 16-CF web[16].
3. Carbon fiber production

The first stage of carbon fiber production is polymer synthesis. Polymer can be synthesized under different polymerization method\[17\]. During polymerization, small molecules or monomers would be chemically combined and form a larger molecules or macromolecules. Hundreds of these macromolecules will form a polymer. The polymerization condition such as different temperature, pressure and catalyst will determine different properties such as molecular weight and diversity in polymer. The following diagram shows that the general polymerization reaction.

![Figure 2: General Polymerization reaction\[17\]](image)

The high temperature and pressure is applied on the monomers to provide enough energy for combination and reaction. Catalysts are used to speed up and activate the chemical reaction\[17\].

Typically, when referring polymer synthesis in PAN precursor, Solution, aqueous suspension, and solvent water suspension methods are usually applied\[18\].

Solution polymerization uses solvent as a heat sink to enhance heat transfer. When choosing such solvent, the monomer, initiator, and the synthesized polymer should be soluble in it. In solution polymerization, initiator will first decompose to primary free radicals. Then those free radicals will react with monomers and convert them into active form. Such step will last until the formation of polymer chain, and Polymerization step ends when the polymer chains are combined\[18,19\].

High molecular weight powdery PAN(HMW-PAN) can also be prepared by aqueous suspension polymerization applying itaconic acid (IA) as comonomer, 2,2'-azobisisobutyronitrile (AIBN) as the initiator and polyvinylalcohol (PVA) as the disperser at elevated temperature (55°C-75°C) for different preparation time (1h-3h) . When compared to other polymerization method, aqueous suspension polymerization has advantages in three aspects. Firstly, the viscosity average molecular weight of produced polymer is higher than that in other polymerization method because chain transfer doesn’t exist. Secondly, the dispersion medium is water, which is more economical. Thirdly, the polymerization system has higher conversion monomers\[20\].

Another polymerization method to prepared HMW-PAN is aqueous deposited polymerization (ADP). Such method is applicable because zero chain transferred coefficient of deionized water and partial solubility in AN. 2,2'-Azobois dihydrochloride (AIBA) is used as an indicator and IA as comonomer. With the increase in initiator concentration and reaction temperature, the molecular weights will decrease. In such technique, the water-soluble AIBA compound will be dissolved in deionized water and dissociated into two radicals under heating. Then copolymerization of AN and other vinyl comonomer will start in liquid phase. HMW-PAN can be obtained through ADP with propagation reactions and chain termination reactions\[21\].

3.1. Spinning

Spinning process is a vital step in CFs manufacturing that converts grinded precursor into continuous fibers. There are three dominant spinning techniques: melt spinning, wet spinning, or dry spinning are most popular and economical spinning techniques in CFs production. In melt spinning, the precursor heated in high temperature and melt first. Then it will be extruded through a spinneret containing small capillaries, and finally the fibers will be produced. When compared to melt spinning, a concentrated solution of the precursor is extruded through a spinneret into a coagulation bath. The
precursor is easier to precipitate and form a fiber when it was produced by the spinneret because the solvent is more soluble in the coagulation fluid. In dry spinning technique, fiber forms by evaporating the solvent in a drying chamber. The spinning methods are different among the precursors[21].

3.2. Stabilization
Stabilization is a step that linear atomic bonding in carbon fibers is converted to the thermally stable ladder bonding, in which the microstructure and shape of the fiber are retained before carbonization[22]. CFs is heated in air to about 200-300℃ for 30-120 mins, the high glass transition temperature in such process ensures the decomposition before softening, and the polymer chains start crosslinking. CFs pick up the oxygen molecules from the air and rearrange their molecular bonding[23]. The temperature and air flow in heating process is varied by different precursor because every precursor has its own exothermic term.

3.3. Carbonization
Carbonization occurs in a oxygen-free atmosphere, where the temperature are progressively increased by a series of furnace. This existence of every oxygen molecule cause the weight loss in CFs, and purge chambers at the exit and entrance of the furnace prevented the oxygen. Carbonization usually first expects in a relatively low temperature furnace at 700-800 ℃ and ends at high temperature furnace at 1200-1500℃. In such process, fiber is continued to be stretched till the end of process. Desired contents of carbon determined the further step, in order to achieve higher content of carbon in the fiber, crystallization of carbon occurred. Fibers carbonized at 1315 ℃ contain 93-95% carbon element, and the latter are graphitized at 1900-2480℃. The modulus of carbon fiber depends on the dwell time and temperature in different furnaces. Carbonization dwell is required to be precise in minutes to control the loss in carbonization[24].

3.4. Surface treatment
Surface treatment is especially important in CFRP, it enhances the connection between matrix resin and carbon fiber. The most common method of surface treatment is pulling the CFs through an electrochemical bath, such as sodium hypochlorite or nitric acid. Those solution rough the surface of the CFs, increases the surface area for matrix bonding and adds chemical group. The second step is
coating, which increases interfacial strength between CFs and matrix resin. Sizing protects CFs while handling and processing into intermediate form and it depends on customer’s desires[24].

4. Conclusion
The reviews identify the development of carbon fiber and its abbreviated manufacturing process. The global carbon fiber market size valued at USD 2.25 billion in 2015, and such market size is expected to grow at CAGR of 10.9% till 2025. As the development of society and improvement of living standards, the application of CFs is also diversified. CFs is not only applied to aerospace and military industry, but also gradually present in human’s daily necessaries, and such industry is still promising in the future.

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