Study on production technology and surface morphology of carbon fiber

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Abstract. Since the 21st century, China's carbon fiber industry has begun to develop rapidly. The research and development of carbon fiber is a major project related to national strategic security. Carbon fiber production technology has been mature, among which PAN based carbon fiber has the largest capacity. However, compared with the imported carbon fiber materials, there is still a certain gap in the performance of domestic carbon fiber materials. The purpose of this paper is to compare the properties of domestic carbon fiber and its composites. Firstly, the production process of carbon fiber is introduced, including monomer polymerization, spinning, oiling, preoxidation, carbonization, graphitization and other steps. Then, the T700 Carbon Fibers of Toray, Japan and two kinds of domestic T700 Carbon Fibers of Hengshen and Weihai were characterized and analyzed, and the surface morphology of three kinds of carbon fibers was compared. It is found that the domestic carbon fiber of Weihai adopts the similar technology of thousand spray wet spinning, and the fiber surface is smooth. However, Hengshen carbon fiber adopts the wet spinning process. There are grooves on the surface of the fiber, which will increase the mechanical meshing force between the fiber and the resin, and have a positive significance for the interface performance of the composite. However, it will increase the probability of fiber defects, such as fine lines, and have a negative impact on its tensile properties and other mechanical properties.

Keywords: carbon fiber, material, production process, surface morphology

1. Research background and significance

1.1. Background
Carbon fiber is a kind of polycrystalline material composed of disordered lamellar graphite crystals arranged along the fiber axis [1]. It is a kind of inorganic polymer fiber with carbon content of more than 90% after high temperature carbonization of organic fiber. The surface layer of carbon fiber material is composed of large and relatively ordered graphite microcrystals, while the disordered and smaller crystals are wrapped in the core, which has a typical "skin core" structure. This structure can effectively reduce the chemical activity on the surface of carbon fiber, and ensure that the fiber has torsion resistance and high strength.
Carbon fiber has many excellent properties [2], such as light weight, high specific strength, high specific modulus, high temperature resistance, small coefficient of thermal expansion, high fatigue strength and good chemical stability. In particular, it has not only the characteristics of carbon materials, but also the flexibility, machinability and excellent mechanical properties of fiber materials. The tensile strength of carbon fiber is about 2-7 GPa, and the tensile modulus is about 200-700 GPa. It is lighter than aluminum, less than a quarter of the weight of steel in the same volume, and its strength is 20 times that of iron.

In recent years, it has been widely used in many fields, such as military and civil, and it is a high-tech fiber material which is encouraged to be developed preferentially at present in China. Carbon fiber can be divided into different types according to the source of raw materials, state, mechanical properties, product specifications, etc. The raw material of viscose carbon fiber is viscose wire, which has better heat insulation and ablation resistance due to the less alkali metal content. However, the manufacturing process is complex, the carbonization yield is only 20%, the cost is high and the output is small. PAN based carbon fiber is the most widely used carbon fiber material, which uses polyacrylonitrile fiber as raw material, with mature production process, high carbonization yield up to 50% and excellent comprehensive performance.

1.2. Significance
Carbon fiber has excellent mechanical properties, but it is rarely used alone as a structural material. Generally, it is processed into two-dimensional woven fabric and other intermediate products or processed into composite materials as reinforcement for use. [3] The so-called composite material means that two or more materials with different properties are optimally combined into new materials according to the performance needs through advanced technology.

At present, the world's major manufacturers of carbon fiber materials, such as Toray, Toyo, Mitsubishi Rayon, hecksell and other companies in the United States, have realized the industrialization of high-performance carbon fiber [4]. But our country is still in the stage of development. As developed countries control high-performance carbon fiber as a strategic material, it restricts the development of carbon fiber in China to a certain extent. Therefore, it is an urgent and significant task to accelerate the industrialization and engineering application of domestic carbon fiber.

2. Carbon fiber production process
Carbon fiber with excellent mechanical, chemical and electrical properties is a very important new material in national economy and national defense construction, known as "black gold". After the 21st century, the production technology of carbon fiber has been mature, among which PAN based carbon fiber has the largest capacity and the most extensive application, and the technology is relatively more mature. The production process mainly includes the following steps: monomer polymerization, spinning, oiling, preoxidation, carbonization, graphitization and so on.

2.1. Monomer polymerization
One-step and two-step methods are used to prepare spinning stock solution. One-step method is to use homogeneous solution polymerization method to directly obtain uniform pan solution, and then to get spinning stock solution after a series of treatment such as washing, de monomer and de foaming. This is the most commonly used and fully researched method in carbon fiber production. The advantages are low viscosity and direct spinning, while the disadvantages are low product yield and difficult solvent recovery it needs washing, refining and other processes.

The two-step process is to prepare pan solid particles through heterogeneous polymerization process, and then the powder is cleaned, dried, crushed and dissolved to prepare even pan solution, and then the spinning solution is obtained through subsequent deionization and defoaming treatment. Compared with solution polymerization, the advantages of this method are that the polymer with higher molecular weight and more uniform molecular weight distribution can be obtained, and the polymerization rate is faster the conversion rate is high. The disadvantage is that it needs to be re
dissolved before spinning. Compared with one-step process, a program is added. At the same time, the separation and drying of Pan solid particles consume a lot of energy.

2.2. Spinning
In the preparation of PAN precursor, the main spinning processes are wet spinning and dry jet wet spinning. Wet spinning is that the spinning solution is directly immersed in the solidified solution after coming out of the spinneret, as shown in the figure below. The method is simple and easy to control. The surface of the carbon fiber prepared by this method has grooves extending the axial arrangement of the fiber, increasing the surface area of the carbon fiber is conducive to the physical engagement of the carbon fiber and the resin, improving the interface bonding performance of the composite, but at the same time, the grooves are also defects on the surface of the carbon fiber, which are easy to produce stress concentration and affect the tensile strength of the carbon fiber.

Dry jet wet spinning is that the original solution flows out from the spinneret head, passes through the air first and then is immersed in the condensate. The spinning speed is fast, the fiber is compact, the surface is smooth, the arrangement and orientation of Pan molecular segments along the fiber direction are optimized, and the tensile strength is higher. However, the disadvantage of dry jet wet spinning is that the spinning solution is easy to flow along the spinneret after the fine flow breaks. It seriously affects the continuity of spinning process. At the same time, the residual organic solvent easily causes the internal defects of the precursor and affects the fiber quality.

2.3. Oiling
After solidification, PAN precursor with excellent and stable performance can be made by at least four times of water bath drawing, water-based oil agent, drying densification, high temperature steam drawing, silicon based oil agent, drying and finalization.

There are two oiling processes in this process. The first oiling process is to prevent the adhesion and cluster of primary raw silk during the densification process. The second mixing of silicon oil agent is to form a protective layer on the surface of the raw silk, reduce the friction loss between the raw silk and the roller in the subsequent process, and at the same time improve the bunching property and antistatic property of the raw silk.

2.4. Preoxidation
Before carbonization, in order to prevent PAN fiber from melting in high temperature, it is necessary to pre oxidize the raw silk. That is to say, the raw silk is placed in the oxidation atmosphere of the pre oxidizer at 200 ~ 300℃, and the molecular chain extends the axial orientation of the fiber to form a trapezoid structure with good thermal stability.

The color of the filament changes from white to yellow, then brown, and finally black. The exothermic reactions are mainly cyclization, dehydrogenation and oxidation. Therefore, the key of preoxidation process lies in temperature control and equipment ventilation. The reaction heat in the furnace should be eliminated in time to prevent fiber fracture caused by local overheating. The principle of preoxidation is to promote the formation of stable trapezoidal structure, reduce the production of small molecular products and improve the carbonation rate.

2.5. Carbonation
After the pre oxidation treatment, the pre oxygen wire should be carbonized twice under the protection of high purity nitrogen. They are low temperature carbonization and high temperature carbonization. The low temperature is generally 300-900℃, and the high temperature is generally 1200-1800℃. In the process of preoxidation, the heat stable trapezoidal macromolecules are crosslinked to form a six membered carbon ring plane with conjugated π bond. With the increase of carbonization temperature, hydrogen, nitrogen, oxygen and other elements are gradually cracked and discharged, and the carbon content in the fiber increases from 60% to more than 90%. Finally, PAN based carbon fibers with disordered graphite sheet structure were obtained.
2.6. Graphitization
If the high modulus graphite carbon fiber is further prepared, the carbon fiber after carbonization is graphitized. The temperature is generally controlled at 2600 ~ 3000°C. With high purity argon as the medium, the internal crystallization of carbon fiber is further oriented under certain tension. Finally, ordered two-dimensional reticulated layered graphite structure fibers are produced, as shown in the figure below. The carbon content also increased to 99%.

![Figure 1. Molecules of graphite layer in carbon fiber](image)

In the graphite layer, the carbon atoms are arranged in a six membered ring. These layers are combined by van der Waals force to form a graphite like three-dimensional structure with a layer spacing of 0.335nm. In the process of preparing high modulus carbon fiber from PAN precursor through a series of heat treatment, the orientation of graphite layer is parallel to the fiber axis. The orientation of crystal layer is the key factor to affect the fiber modulus. The orientation degree of graphite layer is determined by the control of heat treatment temperature and tensile force during the preparation of carbon fiber.

3. Surface morphology analysis of carbon fiber
In this paper, three kinds of T700 Carbon Fibers, Toray, Hengshen and Weihai, were selected to characterize and compare the properties of the fibers and their composites. Scanning electron microscope was used to observe the surface physical state of three kinds of carbon fibers, namely, Dongli, Hengshen and Weihai. The surface morphology of carbon fiber with a scale of 10 μm was obtained, as shown in the figure below.

![Figure 2. The surface physical state of three kinds of carbon fibers](image)
According to the surface roughness of carbon fiber, the wetted specific surface area between carbon fiber and polymer was determined. Furthermore, the interface bonding properties and mechanical properties of carbon fiber reinforced resin matrix composites are deduced qualitatively.

It can be seen from the above figure that the three kinds of carbon fibers are evenly distributed, with a diameter of about 7-8nm. Among them, the surface of Hengshen carbon fiber has obvious grooves, while the surface of Dongli and Weihai expanded carbon fiber is relatively smooth. This is because Hengshen carbon fiber adopts the wet spinning process. During the spinning process, the viscous polypropylene cyanogen solution is ejected from the spinneret and directly enters the solidification liquid. The solidification of the epidermis prevents the solidification liquid from spreading to the inside of the fiber. As a result, the epidermis becomes hard and soft inside, forming a skin core structure. The internal structure is uneven and defective. At the same time, the epidermis collapses inward after the fiber is under traction groove. The existence of grooves increases the specific surface area of carbon fiber, increases the wetted area of carbon fiber and polymer matrix, and improves the interface meshing strength, which plays a positive role in the mechanical properties of composite materials. However, at the same time, the skin core structure and internal defects will also cause the fiber strength to decline, while the expansion of carbon fiber in Dongli and Weihai has no obvious grooves, which is the result of dry jet wet spinning process, In the dry jet wet spinning process, the polypropylene solution is ejected from the spinneret, first passes through the air section and then enters the solidified liquid. In the air section, the solution is viscous and not solidified, and the drafting is smooth and fast. At the same time, the pan molecular chain section is more arranged along the fiber direction, the fiber is dense and uniform, the graphite has high crystallinity, and the strength is also higher. In addition, there are different sizes of block, ball and line on the fiber surface Bumps or spots, which may be treated by electrolysis in the fiber production process.

As a result, the surface active groups and surface area of the fibers were increased. In general, due to the wet spinning process, the surface roughness of Hengshen carbon fiber is greater than that of Dongli carbon fiber and Weihai expanded carbon fiber. There are grooves and bulges on the surface of carbon fiber, which is conducive to increase the surface area of carbon fiber and resin infiltration, improve the mechanical engagement between the two, and then improve the interface performance between the fiber surface and polymer matrix the interlaminar shear strength of composites plays a positive role. On the other hand, because of the existence of grooves, the probability of fiber defects and cracks will be higher than that of the other two fibers, and the tensile strength may be lower than that of the same grade fibers.

4. Conclusion
In this chapter, three kinds of carbon fibers, Dongli, Hengshen and Weihai, were tested and characterized by SEM respectively, and the micro morphology of the three kinds of carbon fibers was compared and analyzed. The surface morphology of the three kinds of carbon fibers was observed by SEM. The diameter of the three kinds of carbon fibers was about 7 μm, which was relatively uniform. The surface of Dongli T700 Carbon fiber is smooth without obvious grooves, and the dry jet wet spinning process is used in the production process. There are obvious grooves on the surface of Hengshen carbon fiber in two kinds of domestic T700 Carbon Fibers, and the orientation is good. The wet spinning process should be adopted, which is relatively mature, and the surface of Weihai carbon fiber is smooth. The dry spray wet spinning process similar to that of Dongli should be adopted.

On the one hand, the existence of surface grooves will increase the fiber roughness and specific surface area. It improves the mechanical engagement and interface performance between fiber and resin matrix, and has a positive effect on the mechanical properties of composite materials. On the other hand, the existence of grooves will increase the probability of fiber crack formation, resulting in high dispersion of physical properties such as fiber strength.

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