UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Físicas y Nanotecnología

Título: State of the art in the use of carbon fibersand their mechanical properties

Trabajo de integración curricular presentado como requisito para la
obtención del título ingeniero en Nanotecnología

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Abstract

The present work is based on the investigation and collection of bibliographic data about carbon fibers as reinforcing material in composites. Therefore, for its understanding, a compilation of historical, conceptual and investigative data was carried out on these. Where you get to know in depth the origin, obtaining, handling, manufacturing and properties of these materials, in addition to their applications today.

Carbon fibers currently have very useful properties that when combined with different materials provide unique properties to different compounds. Carbon fibers were developed in the nineteenth century for bulbs, since then they have been perfected in their properties and purity. Although its use entails some inconveniences such as production cost or the polluting residues that its manufacture entails, carbon fibers are widely used around the world. At present these are used in very varied industries such as: aeronautics, motor racing, wind energy, and boats among others. The use of carbon fibers as a reinforcing material in the development of new materials contributes to the optimization of resources, technological and scientific development in various fields of society.

Abstract

El presente trabajo se basa en la investigación y recopilación de datos bibliográficos sobre fibras de carbono como material de refuerzo en composites. Por ello, para su comprensión, se realizó una recopilación de datos históricos, conceptuales e investigativos sobre estos. Donde conocer en profundidad el origen, obtención, manipulación, fabricación y propiedades de estos materiales, además de sus aplicaciones en la actualidad.

Las fibras de carbono tienen actualmente propiedades muy útiles que cuando se combinan con diferentes materiales proporcionan propiedades únicas a diferentes compuestos. Las fibras de carbono fueron desarrolladas en el siglo XIX para bombillas, desde entonces se han perfeccionado en sus propiedades y pureza. Aunque su uso conlleva algunos inconvenientes como el coste de producción o los residuos contaminantes que conlleva su fabricación, las fibras de carbono son muy utilizadas en todo el mundo. En la actualidad estos se utilizan en industrias muy variadas como: aeronáutica, automovilismo, energía eólica y embarcaciones entre otras. El uso de fibras de carbono como material de refuerzo en el desarrollo de nuevos materiales contribuye a la optimización de recursos, desarrollo tecnológico y científico en diversos campos de la sociedad.

Acknowledgements

At the conclusion of this wonderful stage of my life, I want to, first, thank Our Heavenly Father for giving me intelligence, wisdom, for guiding me, protecting me, and giving me health to be able to successfully complete this career. I must place on record my most sincere thanks to Yachay Tech University and especially to the Faculty of Physical Sciences and Nanotechnology for having welcomed me into their establishment.

There are many people who have contributed to the process and conclusion of this work, first of all, I want to thank my thesis director Professor Chacón Torres Julio C. for his personal and institutional support, for his contributions to be able to elaborate my thesis. Thanks for your patience in explaining and guiding me through the entire. You have encouraged me to continue with the process, teaching me with dedication and care. Thanks to all the teachers I had at Yachay Tech, they transmitted their passion for research and desire to learn to me.

A very special thanks to my parents who walked with me at all times giving me support, strength, their unconditional love, and they gave me words of encouragement so that I could go ahead, and fulfill my goals. Every day they gave me the best advice of my life that made me realize that studying was the best way to become a successful person because without their words I might not have been able to be a professional. I am very happy to be able to thank them for the trust they placed in me, because at no time did they show any doubt before me, on the contrary, they were always giving me words of encouragement, and when I felt tired they were there to help me get up again and not give up my goal set.

I want to thank my friends and colleagues who were like my second family. They were always present in highs and lows throughout my career. I am very happy to have met them because they were and are a support in the academic field and personal life.

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Chapter 1

Introduction

The application of carbon fibers as a reinforcing material in composites is one of the most important discoveries of the last century. This is due to the fact that thanks to their hardness, weight, tensile strength, among other characteristics, they have a wide field of application.[1] Today's technology has advanced by leaps and bounds, having ever greater requirements. This has involved in the search for materials with greater mechanical, finish, and chemical resistance, as well as great durability and lower weight. This entailed progressive reduction of metals in the composites and the application of different types of fibers. It is here that carbon fiber was found to be the "jewel in the crown".

Carbon fibers began to be developed in the 19th century and for many years their only use was as a filament for light bulbs, with a low yield in carbon content. Almost a century later, it began to give more importance and to investigate how to increase its performance and its possible applications. This achieved that the fibers are currently positioned as one of the best materials as a reinforcing material. Attracting the interest of not only the scientific community but of different types of industries, including the arms market.[1] For the year 2012, the estimated demand for the carbon fiber market was 1700 million US dollars with an estimated growth of 12%. The greatest demand for carbon fiber comes from the aerospace and aeronautical industry, automotive industry, and wind power.[2]

1.1 Justification

In Ecuador, in recent years, the need to improve the country's productive system has been promoted. One of the main focuses was the support to the universities to generate research and that in such a way that the productive system was improving in knowledge and generation of ideas.[3]

The country's production policies are focused on the production and export of raw materials, creating the need to catch up with other countries that have ventured into new production models such as the field of research and production of new materials. Likewise, a transforming model must be established that is capable of offering a raw material with added value or a derivative of this more efficient and competitive.[3]

Due to the aforementioned, it is imperative to compile information about carbon fibers, focusing, in this case, on the properties that they provide to different materials. Consequently, the purpose of this research work and bibliographic compilation is to generate interest in the Ecuadorian industrial environment.

Therefore, in our country, it is necessary to encourage research on new materials (carbon fibers), and thus reduce the technological gap with first world countries and join the trends of world research. In order to implement this type of technology in the industrial sector and with the advancement of the years progressively stop depending on imports.

1.2 Problem Statement

The carbon fibers are a relatively new material, since we have been exploiting it in its entirety for less than a century, while other materials such as metals have been in the market for thousands of years with their developments and applications. This has been one of the main throwbacks in the way of carbon fibers. This has led to the recent "boom" in the application of fibers in fields as varied as medicine, sports, and even the arms race in different countries.

One of its main limitations today is supply and demand. Many companies seek to improve the quality of their products (properties) with the partial or total implementation of these fibers. This has led to a huge increase in demand, while supply has not developed at the same speed. Another limitation is the complexity of its development. Very specific conditions and parameters are needed to obtain good quality fibers. In addition, these parameters are specific for each product to be developed, leading to their little applicability for mass production. All these factors have led to a high production cost, limiting its large-scale development.

This work seeks to show how the production of carbon fibers works from its theoretical basis, precursors, characterization and applications in composites. In order to help spread knowledge, ensuring that this technology is incorporated into new products every day, improving their quality, and properties. At the same time, contributing to the development of production sources, which will lead to a reduction in their production cost over the years.

1.3 General and Specific Objectives

1.3.1 General Objective

- Conduct scientific research on carbon fibers by using search engines for scientific articles (Google scholar, scopus), repositories, and scientific journals to review how small changes in its precursors, manufacturing methods, and functionalization agents affect the physical and chemical properties of the carbon fibers.

1.3.2 Specific Objective

- Understand how the proper application of carbon fibers can improve the physical and chemical properties.
- Analyze the surface morphology of carbon fibers.
- Analyze the mechanical performance of carbon fibers.
- Disseminate knowledge about carbon fibers, their properties, and characteristics to help improve technological development and applicability.

1.4 Methodology

To carry out this work, a qualitative-documentary research methodology was used. By means of a systematic data survey, a bibliographic compilation of existing literature on carbon fibers and their main applications in the industry was made. This search was carried out through search engines in the virtual network of scientific articles (google Scholar, Scopus, Mendeley), repositories, scientific journals.

For the development of this research, first a large amount of data about carbon fibers was collected, their properties, their applications, advantages, and disadvantages. Subsequently, the information was classified according to its importance. For this, classification parameters such as: year of publication, scientific impact, popularity, and topic in which the research is applied were used.

Subsequently, the classified information was subjected to a filter to know if it was relevant in the review. If the papers, books, or other material was not adequate enough, they were discarded and proceeded to the previous step, which is to find suitable material. Once the articles with the greatest impact were selected, they were separated by topics: basic concepts, history, properties, procedure, manufacturing, among others.

Once all the information is available, we proceed to write the history of nanomaterials, their incorporation as a branch of science until they reach the present time, where they have high quality and purity carbon fibers. Later, the properties of carbon fibers, their composition and structure are analyzed in detail. In order to achieve a great understanding of the possible applications and advantages that this great material offers us.

Therefore, what we want to achieve with this work is the compression of the applications in composites that carbon fibers provide us. Like these, although they have a high production cost and complex manufacturing, they are the material of the future in more than one branch such as aircraft, aerospace, wind energy, and automotive among other applications.

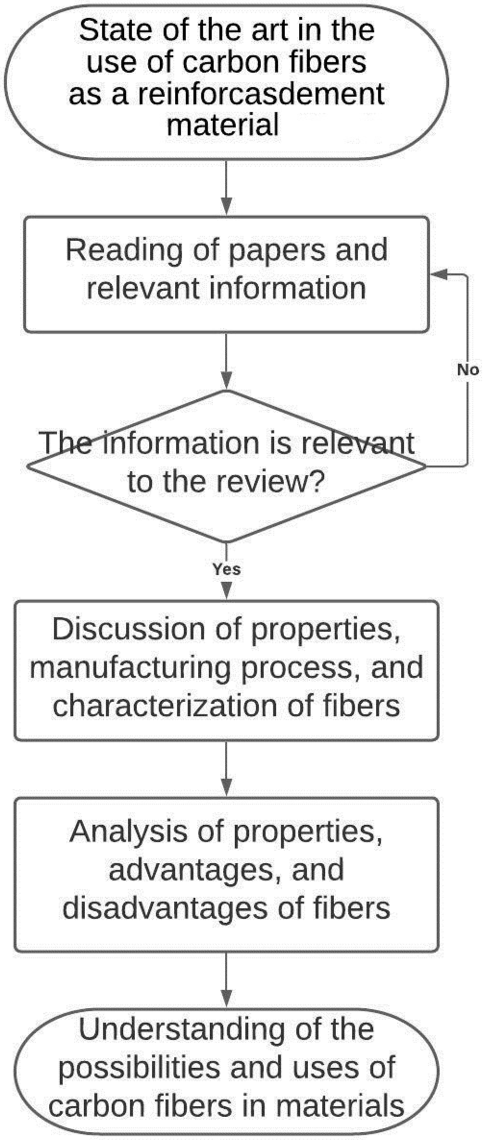


Figure 1.1: Flowchart of state of the art in the use of the carbon fibers as a reinforcement material in composites

Chapter 2

Theoretical Fundament

The Nanotechnology refers to that technology that is implemented at the nanoscale and has applications in the real world. In other words, it is the manipulation of matter on a nanometric scale or manipulation with at least one dimension of the size between 1 and 100 nanometers. The term nanotechnology encompasses a wide range of techniques, tools, and applications, that allow us to develop nanostructures and nanostructured materials with greater applicability and sustainability.[4]

Nanotechnology is a relatively recent science, it emerged in the last century and has been gaining importance with the development of new methods of research, characterization, and manufacturing in materials. One of the fathers of Nanotechnology and who offered its theoretical origin is Richard Feynman, Nobel Prize winner in physics (1965). On December 1959, at the congress of the American Physical Society, Feynman gave his famous lecture entitled "There's Plenty of Room at the Bottom." There he was the first to refer to the possibilities of nanoscience and nanotechnology in a speech, in addition to describing the possibility of synthesis via the direct manipulation of atoms. This speech is frequently cited as a source of inspiration for the nanotechnology field.[4]

However, the term Nanotechnology was used for the first time in a conference in 1974 by the Japanese scientist Norio Taniguchi of the Tokyo University of Science, to describe the processes of production of thin-film deposits and ion-ray devastation in semiconductors, with a dimensional check in the order of nanometers. In the 80s the idea that nanotechnology was an area dominated by determinism, which was based on the individual handling of molecules and atoms, proffesor

Figure 2.1: Richard Feynman[5]

K. Eric Drexler studied it conceptually in depth. He instilled and promoted the importance of nanoscale phenomena. In 1986 Eric Drexler was co-founder of The Foresight Institute, this institute created with the purpose of helping to increase the understanding of the concepts of nanotechnology, its principles and applications.[4]

Once the bases for nanotechnology were founded by these great scientists, certain technological discoveries marked a notable boost at the beginning of the eighties with two important developments: the invention of the Scanning Tunneling Microscope (STM) that is an instrument for revealing the topographic structures of the surfaces at the atomic level and later the discovery of clusters that consist of a small number of atoms, at most in tens. These nanoclusters can be composed of one or more elements, and are typically less than 2 nm in size.

Gerd Binnig and Heinrich Rohrer also invented the atomic force microscope (AFM) in 1986. This microscope is a mechano-optical instrument capable of detecting forces on the order of nanonewtons. By tracking a sample, it is able to continuously record its topography using a tip point. The tip is attached to a very flexible cantilever of only about 200 μm.[6]

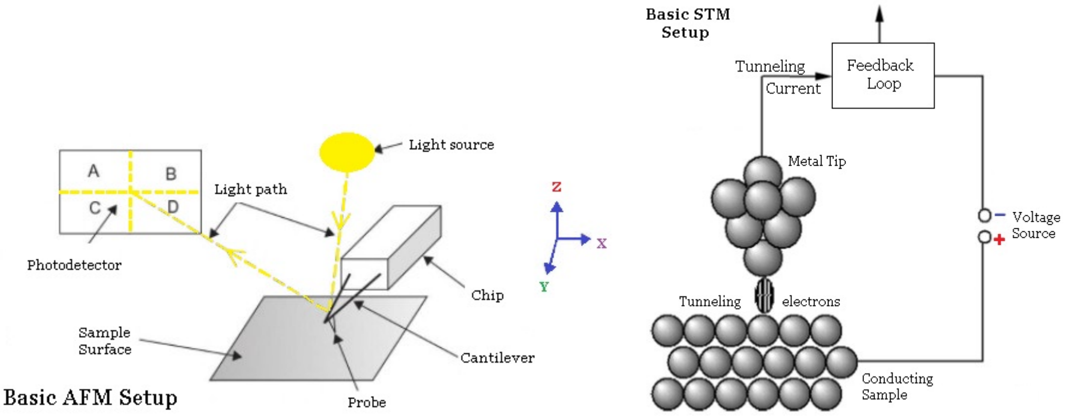


Figure 2.2: Basic AFM setup[6] —— Basic STM setup.

One of the first structures discovered with the help of these instruments was Fullerenes, in 1985. Harry Kroto, Richard Smalley and Robert Curl won a Nobel Prize for their discovery in 1996. Fullerenes are molecules made of carbon that can adopt a geometric shape reminiscent of a sphere. These are similar to graphite, composed of linked hexagonal ring blades, but also contain pentagonal and heptagonal rings, preventing the blade from being flat. These are the third known stable molecular form of carbon, after graphite and diamond.[7]

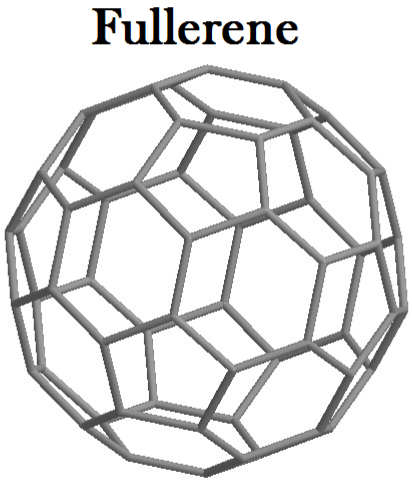


Figure 2.3: Fullerene C_{60}. Image extracted from: Principles of fullerene reactivity[7]

Carbon nanotubes were subsequently discovered by Sumio Iijima in 1991, this made him creditor of the inaugural Kavli Award for Nanoscience in 2008. In the 2000s, Nanotechnology gained increased scientific, political, and commercial attention that led to research and progress. Doubts and controversies arose about definitions and possible implications. The commercialization of products based on advances in nanoscale technologies began to emerge. At this point, nanotechnology was already established as a branch of science and research.[8]

On the other hand, carbon fibers began their development in 1860. The first to develop carbon fibers was Joseph Swan for the incandescent lamp filament. Later, cotton threads and bamboo fibers were baked at high temperatures, charring them into a carbon fiber filament that was used in the first incandescent bulbs heated with electricity by Thomas Edison in 1879. The next notable breakthrough was nearly a century later in 1958, where Roger Bacon created the first carbon fiber of high performance. These fibers were made by heating cellulose fiber until charred. This process was inefficient, since the fibers produced contained 20 % carbon and also had low strength and stiffness.[9]

In the early 60s, Dr. Akio Shindo of the Japan Industrial Science and Technology Agency developed a process using polyacrylonitrile (PAN) as a raw material. This produced a carbon fiber containing approximately 55% carbon. In 1960 Richard Millington developed a method to produce high carbon fibers (99%), using Celulose Fiber (rayon) as a precursor.[1] These carbon fibers were strong enough because they had high Young's modulus and tensile strength. In 1963 W. Watt, LN Phillips and W. Johnson succeeded in developing a potential high strength fiber. The process was patented by the United Kingdom Ministry of Defense. During the 1960s, new raw materials were found, which led to the production of carbon fibers made from a pitch derived from oil processing. These fibers contained approximately 85% carbon. At the end of the 1970s, new kinds of yarn were developed, offering the global market a higher tensile strength and a higher modulus of elasticity.[1]

Since the final carbon fibers contain almost 100% carbon, any fibrous material with a carbon backbone could be used as a precursor, which would yield carbonaceous residue upon heat treatment. Many naturally occurring materials such as cotton, jute, linen, sisal and man made polymers like polyester, polyamides, polyvinyl chlorides, polyvinyl alcohol phenol resins, among others, have been tried as possible precursors for carbon fiber manufacture. Little by little, carbon fibers were gaining popularity until they found one of their main applications in the aerospace area, first in military aircraft and then in civil aircraft.[9]

2.1 Theory behind of Nanomaterials

For a better analysis of Nanomaterials, we must first understand that due to their small size 1 - 100 nm they have different properties, characteristics, and dimensions than macroscopic materials. The nanostructures are conformed by clusters, nano-wires, nanotubes, quantum dots, nanocrystals among other specific structures. The physical and chemical properties of materials change depending on whether we consider these materials are bulk-materials or atomic-molecular materials of the same structure. It means that the nanostructured materials have chemical and physic properties that are tuned by governing their size and shape. It provides nanomaterials with unique applications.[10]

2.1.1 Dimensions in Nanomaterials

The nanomaterials can be classified into: zero-dimensional, one-dimensional or two-dimensional materials. The reason for the changes in the electronic and optical properties of the nanomaterial is that if we reduce the size of the material, the electronic wave functions are being more tightly confined. It means that the changes in particle size modify the band-gap and band structure of the material.[10]

- **Zero Dimensional** materials have all the dimensions in the range of nanoscale. Electrons are confined in all three dimensions. If we increase the confinement in this dimension, the coulomb-induced mixing of states becomes more difficult. Increase the Coulomb energies and electrons and holes become frozen in the lowest energy states.[10] 0D nanostructures are fullerenes, clusters, atomic aggregates, and quantum dots among others.[11]

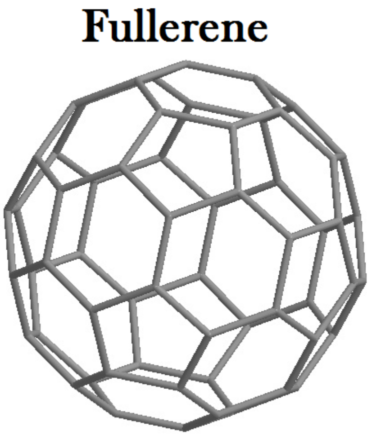


Figure 2.4: 0D material - Fullerene C_{60}. Image extracted from: Principles of fullerene reactivity[7]

- **One Dimensional** materials have one dimension outside the nanoscale >100 nm. Electrons are confined in two dimensions. In this case, the size of nanoparticles become smaller than the Broglie Wavelength leading that the energy levels are discrete similar to atoms. The band gap increases and the spectrum absorption is shifted.[10] 1D nanostructures are graphene nanoribbons, nanobars, carbon nanotubes, and nanowires among others.[11]

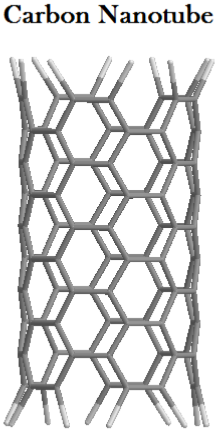


Figure 2.5: 1D material - Carbon Nanotube

- **Two Dimensional** materials have two dimensions outside of the nanoscale >100 nm. Electrons are confined in one direction and behave like in a bulk material. They are mainly thin films with the thickness of nanometers. They are usually deposited on bulk materials, for this reason their properties are dominated by surface and interface effects.[10] 2D nanostructures are graphene (also two layered graphene), nanolayers, and nanofilms among others.[11]

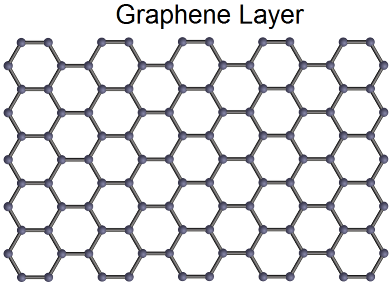


Figure 2.6: 2D material - graphene Layer

- **Three Dimensional** materials have all dimensions outside of the nanoscale. The electrons are not confined and they can move freely. They are not confined to the nanoscale and have all dimensions at the macroscale. This kind of materials contains dispersion of nanoparticles, graphite, polycrystals, aerogels, bulk materials, and bulk powders among others.[11]

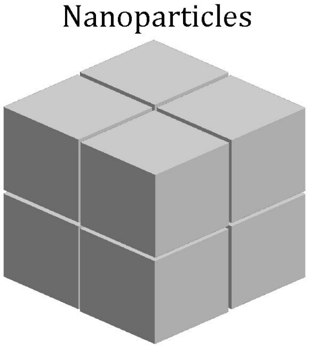


Figure 2.7: 3D material - Nanoparticle

2.1.2 Atomic Orbital

The atomic orbital is the space region independent of time in which there is a greater probability of finding an electron. There can be a maximum of two electrons in an atomic orbital. An atomic orbital is classified by sublevels s, p, d, and f. The orbitals of these sublevels contain different shapes.[12]

- **S orbital:** this orbital is characterized by having a spherical shape. This cloud is denser the closer it is to the nucleus and more dispersed the further it is.[12]
- **P orbital:** these orbitals consists of two lobes that are projected along an axis, these have the same shape and energy, but with different orientation.[12]
- **D orbital:** these orbitals have various shapes and orientations. Four of them are shaped like 4 lobes of alternate orientation, and the last one is a double lobe surrounded by a ring.[12]
- **F orbital:** this orbital has a multilobular shape. Which can be described by adding a nodal plane to the shapes of the d orbitals.[12]

2.1.3 Hybridization

The hybridization can be defined as the concept of mixing two atomic orbital with similar energy levels to form a newly hybridized orbital. These new orbital influences molecular geometry and bonding. Based on the types of orbitals involved in mixing, the most common hybridization are sp^3, sp^2, sp.[13]

sp^3 hybridization

In the case of Carbon-Carbon the hybridization available are sp^2 and sp^3. In the case of sp^3 hybridization one S orbital and 3 P orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, it can be seen in the Fig. 1.7 left. The type of hybridization is called a tetrahedral hybridization. One example is diamond, where its transparent appearance corresponds to the fact that electrons be excited out of the valence band into the conduction band with a wavelength in the ultraviolet range.[14]

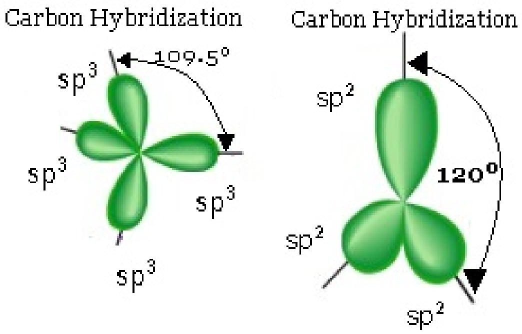


Figure 2.8: SP3 and SP2 Hybridization of C-C bonds[14]

sp^2 hybridization

In the case of sp^2 hybridization one S orbital and 2 P orbitals belonging to the same shell of an atom mix together to form three new equivalent orbital, it can be seen in the Fig. 1.7 right. The type of hybridization is called trigonal hybridization. One example is graphite. Between the layers, the π-orbitals give rise to weak Van-der-Waales forces. As a result, graphite is one of the softest materials known and is used in pencils.[14]

sp hybridization

sp hybridization can be defined as the combination of an S orbital and a P orbital, to form 2 hybrid orbitals, with an angle of 180º. It is found in compounds with triple bonds such as alkynes.[13]

2.1.4 Energy bands

The electrons of an atom occupy atomic orbitals, and each of these has discrete energy levels. At the moment of having two or more atoms, the atomic orbitals overlap. It's know that the **Pauli Exclusion Principle** states that two electrons cannot have the same quantum number.[15] Then each atomic orbital is split into two molecular orbitals of different energy. This allows the electrons to occupy the new orbital structure without having the same energy. Considering a large number of atoms in a macroscopic piece, the number of orbitals will also be very large. Then these will be very closely spaced in energy. If we consider the adjacent energy levels, they are so close that they can be considered continuous, as an energy band. The formation of bands corresponds to the valence electrons in the atom, these are those that participate in electrical conductivity and chemical bonds. There are three principal bands valence band, conduction band, and bandgap.[16]

Valance band

The Valence band can be defined as the outermost electron orbital of an atom at zero kelvin or as the highest range of proton energies in which electrons are normally present.[16]

Conduction band

The conduction band can be defined as the lowest range of empty electronic states. When an electron is excited it can jump from the valence band to the conduction band. When electrons are in this band they have enough energy to move freely in the material. This flow of electrons creates the electric current.[16]

Bandgap

The band gap is the difference in energy between the highest point of the valence band and the lowest point of the conduction band. The band gaps are excess energy ranges that are not covered by any bands, as a result of the finite widths of the energy bands.[16]

Band theory is used to explain the physical properties of solids, such as optical absorption and electrical resistivity. The range of energy levels that electrons can have or may not have is known as Electronic band structure.[18]

Density States

The density of states gives us information about the availability of states at each energy level. A high value in the density of states corresponds to a high number in the available energy states. On the other hand, if we have a low value in the density of states, it means there are no energy states available for occupation. Dos calculations can determine the spacing between energy bands in semiconductors.[18]

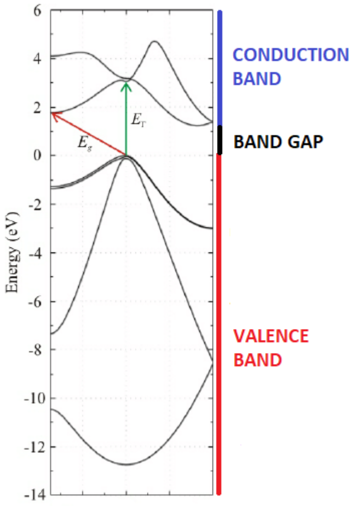


Figure 2.9: Electronic Band Structure for Si. Image extracted from: Photonic integrated circuit (PIC) devices for inter and intra-chip optical communication using GeSn alloy layers grown on Silicon substrates[17]

2.1.5 Yield Strength

The yield strength is the stress corresponding to the yield point (limit of elastic behavior and beginning of plastic behavior). After this point, the material is permanently deformed and will not return to its previous state. The yield strength is used to determine the upper limit of a load of some material without deformation.[19]

2.1.6 Tensile Strength

Also called ultimate tensile strength (UTS), the tensile strength is the maximum load that withstands a material before it stretches and breaks. It is an intensive property, its value does not depend on the size of the sample, but on structural factors such as defects, temperature, and shape of the structure. It is the highest point on the stress-strain curve showed in the Figure 2.10[19]

2.1.7 Young's Modulus

Young's modulus is a parameter that characterizes the behavior of a material. It allows knowing the elasticity of a material, (depending on the direction in which a force is applied). Its value is a constant independent of the effort provided it does not exceed a maximum value called the yield strength. The Young's modulus is different for various materials. Young's modulus or longitudinal modulus of elasticity can be found empirically by tensile testing of the material. It is a parameter that manages to reveal the behavior of a material depending on the type of force applied to it and the consequent increase or decrease in the length of that material. To find it, we need to obtain the relationship that occurs between the stress applied to an object in its longitudinal axis (σ) and the deformation measured in the same axis (ε). This value corresponds to the measures of its elastic behavior and predicts the stretching of a given material.[20]

$$E = \frac{\sigma}{\varepsilon}$$

Where E= correspond to the Young's modulus[20]

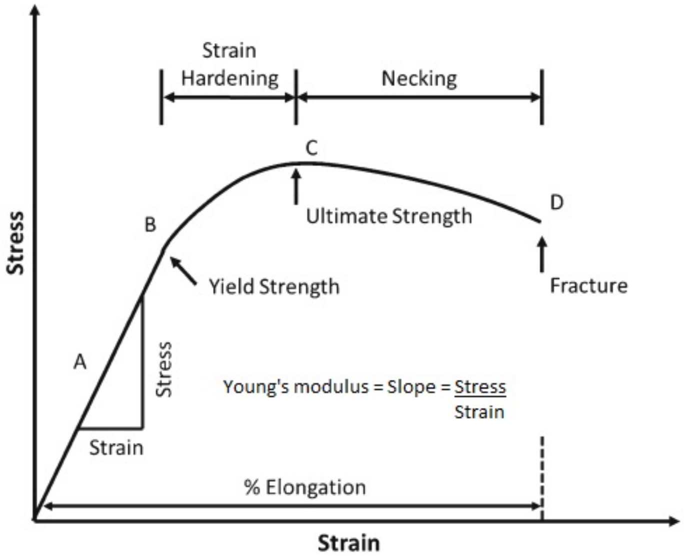


Figure 2.10: Stress–strain curve. Image extracted from: Plasticizer Effects on Physical–Mechanical Properties of Solvent Cast Soluplus Films.[21]

2.2 Nanomaterial Synthesis Process

Its known that all matter is made up of atoms and molecules. Knowing the way things are built gives us very important knowledge to understand the properties of materials. There are two opposite but complementary approaches to the manufacture of nanomaterials. The first is the top-down strategy of miniaturizing components and materials from bulk material. The other way is a bottom-up strategy, it consists in build complex structures atom by atom or molecule by molecule.[22]

2.2.1 Top-Down Approach

The Top-Down strategy consists in the manufacture of nanomaterials from larger-scale materials that are gradually reduced until reaching the nanometric scale.[22] An example of this process is the graphene produced by Andre and Konstantin. This earned them the Nobel Prize in Physics in 2010. Both succeeded in reducing graphite (top-down process) to a one-nanometer-thick monolayer of graphene. They achieve this, removing flakes from bulk graphite with sticky tape repeatedly times. The final flakes have just one atom thick.[23]

2.2.2 Bottom-up Approach

The Bottom-Up strategy consists of building structures, atom by atom or molecule by molecule. This kind of technique uses physical and chemical methods to assemble the basic units (atoms, molecules) into larger structures. The degree of miniaturization achieved by this technique is higher than that which can be achieved with the top-down strategy.[22]

An example of this is carbon nanotubes manufacture, where these can be manufactured by (CVD) chemical vapor deposition. The nanotubes grow from a catalyst metal and obtain carbon from the gases used.[24]

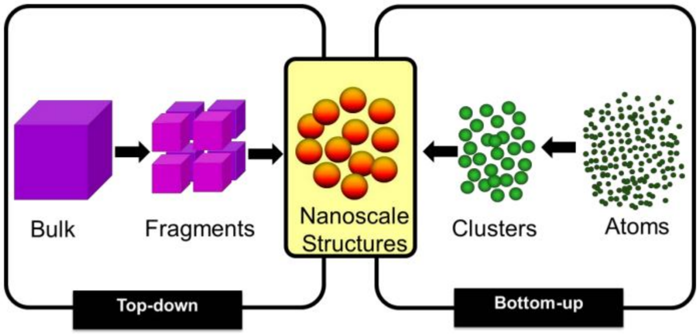


Figure 2.11: Top-down and Bottom-up nanofabrication synthesis. Image extracted from: Dense plasma focus-from alternative fusion source to versatile high energy density plasma source for plasma nanotechnology[25]

2.3 Nanomaterial Properties

One of the most important things about nanomaterials is their properties. The nanomaterial properties can change with very small variations in manufacturing temperatures, pressure, reaction rate, surface area, among other parameters.[26] In the case of carbon fibers can be considered some characteristics and properties derived from these general properties as High Strength to weight ratio, Rigidity, Corrosion resistance, Electrical Conductivity, Fatigue Resistance, Good tensile strength, Fire Resistance, Thermal Conductivity, Thermal expansion, Biologically inert, and X-Ray Permeable. These properties will be explained in the next sections.[27]

2.3.1 Thermal properties

The thermal properties of nanomaterials can be affected by the increase in the surface area and surface energy. Also, if the nanoparticle size changes, the interatomic spacing has an effect on the material properties. One example of this can be observed in the gold nanoparticles (AuNPs), in the particles sizes less than 10 nm the melting point decreases rapidly.[10]

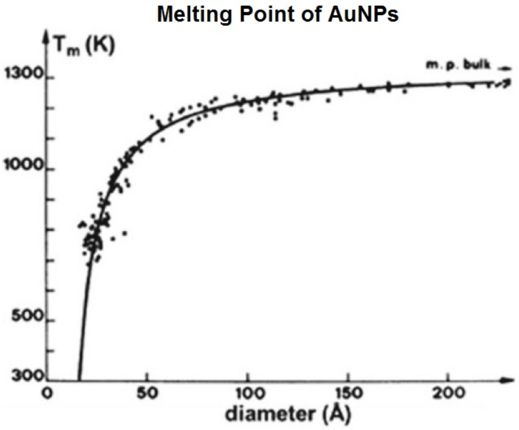


Figure 2.12: Melting Point of AuNPs. Image extracted from: Nanostructured Materials[10]

2.3.2 Chemical properties

The changes in particle size affect the structure, and it is due to its the changes in electronic properties. In small atomic clusters, the ionization potential is higher than for the corresponding bulk material. The big surface area and the potentially different crystallographic structures may lead to an alteration in chemical reactivity. This structural change due its size is accompanied by an extraordinary increase in catalytic activity.[10]

2.3.3 Mechanical properties

The ease of formation or the presence of defects within the material affect mechanical properties such as toughness. At the time of reducing the size, the ability to withstand such defects is difficult and the mechanical properties are altered. Nanometric structures have different properties compared to bulk structures in terms of atomic structure and arrangement, leading to very different mechanical properties.[27]

2.3.4 Magnetic properties

The magnetic nanoparticles have a lot of applications like color imaging, ferrofluids, magnetic location, bioprocessing, among other great applications. The large surface area results in a substantial proportion of atoms having a different magnetic coupling with neighbor atoms.[10]

2.3.5 Optical properties

The transitions between the states produce optical emission and absorption. The metals and semiconductors show changes in optical properties like particle size and color. An example of this are gold nanoparticles that have a deep red color which becomes progressively more yellow as the particle size increases.[10]

2.4 Characterization techniques

The characterization techniques are used to study properties mentioned that will allow us to know the structure and morphology. The parameters analyzed by these techniques are very useful in order to realize the correlation between the properties of the nanomaterials and their structure.[26]

The characterization techniques that we are going to cover in this thesis are Raman, Atomic Force Microscopy (AFM), X-ray Diffraction (XDR), Absorption Spectroscopy (UV-vis), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), and Scanning Tunneling Microscopy (STM).

2.4.1 Raman Spectroscopy

Raman spectroscopy is one of the techniques that is performed on the material in an inelastically scattered light examination to determine rotational, vibrational, and other low-frequency modes of interaction between molecules.[28] Its technique gives the characteristic of the analyzed material, without any alteration of the surface, that is, it is not destructive. The scattered light presents different frequencies to the incident radiation, which is why it provides information on the composition of organic and inorganic materials. These new frequencies + vr and –vr characteristics of the chemical nature and the physical state of the sample and independent of incident radiation, which are equivalent to energy variations.[29]

The working principle consists of the transfer of energy between the photon and a molecule inelastically. If the molecule is excited to a higher energy state, the incident photon loses energy and its wavelength increases, which is called Stokes Raman scattering. On the contrary, if the molecule is excited to a lower energy state, the photon gains energy and its wavelength decreases, which is called Anti-Stokes Raman scattering. Each material have characteristic values of its polyatomic structure and the nature of the chemical bonds that form it. The Raman spectrum collects these phenomena representing the scattered optical intensity as a function of the normalized wave number.[29]

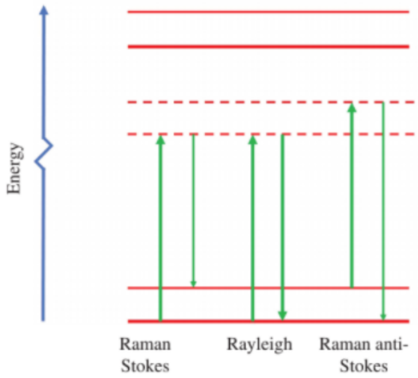


Figure 2.13: Diagram of Raman scattering process. Image extracted from: Modern Raman spectroscopy: a practical approach[29]

The Raman spectroscopy can bring us the structural fingerprint, by which can be identified the molecules that compose it. It is a very useful tool that helps to discover if there are any contaminants in the sample (carbon fiber). Also, another important characteristic is a non-destructive method to analyze composite materials in situ. The Raman bands in graphitic materials have a letter notation like: G-, D-, D'-, 2D-lines among others. These bands can represent hexagonal ring structures, symmetry or disorders structures, degree of graphitization.[28].

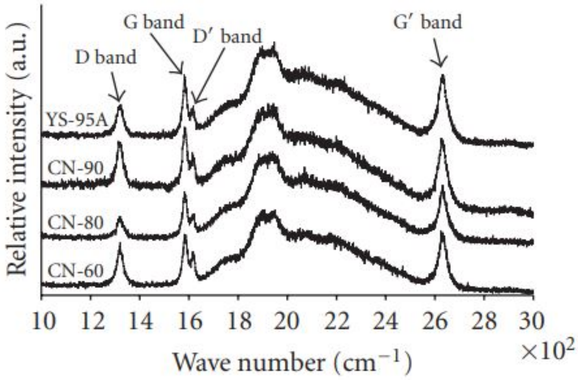


Figure 2.14: Example of spectra with D, G, D, and G Raman bands in carbon fibers. Image extracted from: Raman Spectroscopy for the Nondestructive Testing of Carbon Fiber[28]

2.4.2 Scanning Tunneling Microscope (STM)

The Scanning tunneling microscope (STM) is an instrument for revealing the topographic structures of the surfaces at the atomic level. It was developed in 1981 by Gerd Binnig and Heinrich Rohrer (of IBM Zürich). An STM has an excellent resolution, it has the capability of individual atoms can be observed within materials. The tunnel effect concept is used for its operation and its working principle is based on a conductive tip that is placed very close to the surface to be examined. A bias current is applied between the surface and the tip, it can allow electrons to pass to the other side by quantum tunneling. The resulting tunneling current is a function of the tip position, the applied voltage, and the local density of sample states. A recurring problem with this procedure is that it requires spotless and stable surfaces.[30]

There are 2 modes of operation, constant current and constant height. In constant current mode, the voltage that controls the height of the tip is recorded while the tunneling current is kept at a predetermined level. In constant height mode changes in tunnel current are mapped directly. The separation between the tip and the sample always be between 4 and 7 Angstroms.[30] The working principle can be appreciated in Figure 2.2: Basic STM setup.

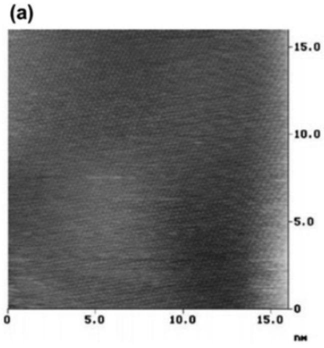


Figure 2.15: Atomic-scale STM image of untreated ultrahigh-modulus carbon fiber surface. Image extracted from: carbon fibers book[1]

The scanning tunneling microscopy (STM) is used to take two-dimensional images of carbon fibers at the nanometric level. It can bring us 0.1 nm of lateral resolution and 0.01 nm of depth resolution. The analysis of carbon fibers with its technique can show the surface structure (if it is: bulk) or if it has microstructures. As this device has a high magnification, it also allows us to observe the atomic resolution of the fibers, where the carbon atoms generally stand out as bright points. This can provide information about the hexagonal structure or the distance between atoms of the fibers.[31] In Figure 2.15 is appreciated an example of ultra-high-modulus carbon fibers by STM, where Atomic-sized spots can be observed.

2.4.3 Atomic Force Microscopy (AFM)

The atomic force microscopy (AFM) is an instrument to give topographic image of a surface, it allows obtaining 3-dimensional images of a solid surface with a high resolution (nanometric). The reason for its high resolution is that it is capable of detecting forces of the order of the nanonewtons. It uses a tip to track a sample by continuously recording its topography. The tip is located at the end of the cantilever arm of 100 to 200 microns long. The force between the tip and the surface of the sample causes the cantilever to be flexed, while a detector measures this flexion that occurs as the tip sweeps the surface and thus a topographic map is obtained. Depending on the type of sample to be characterized, we have 3 modes of use: contact AFM, non-contact AFM, and tapping mode.[32]

This microscope is generally used for the surface characterization like investigate the topographical changes, studies of adhesion forces, characterization of elasticity, indentation of soft materials, measurement of mechanical forces, among others. An advantage is that it does not need high vacuum, high sample preparation, that it is conductive or coated unlike other microscopes.[33] The working principle can be appreciated in Figure 1.1: Basic AFM setup.

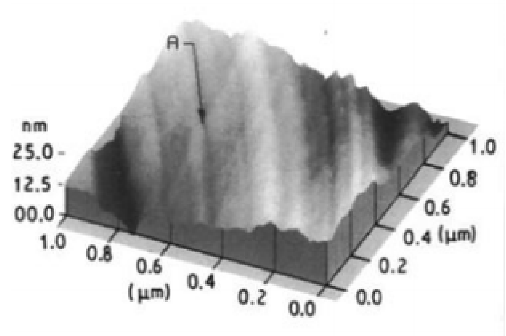


Figure 2.16: AFM image of untreated Cellion 6000 carbon fiber. Image extracted from: carbon fibers book[1]

The atomic force microscopy (AFM) is especially useful when a detailed surface of carbon fiber is needed. It is very similar to STM but is preferable to use the AFM since it requires less preparation in the sample, in addition it can be used both in conductors and insulators, therefore the carbon fibers do not need any coating.[33] In Figure 2.16 corresponds to an example of an AFM image of untreated Cellion 6000 carbon fiber, it can be appreciated the axial grooves were irregular spaced by approximately 40–120 nm and have a depth distribution from 1 to 7 nm.

2.4.4 X-ray Diffraction (XRD)

The X-ray Disfraction (XRD) is non-destructive and experimental technique to study the crystal structure of the material (regular sets of atoms). This technique allows us to know crystalline phases, chemical composition, size, shape, and internal stress of the material. X-rays are used because their wavelength ($10y10^{-12}nm$) and energies between 0.1 y 100 keV. Also, the visible light has a length much greater than the space between atoms. When the x-ray beam hits an electron, it produces spherical waves (elastic scattering). Most waves cancel by destructive interference (when the phase difference is 180 degrees), while a small percentage adds by constructive interference (waves are in phase, need the difference of their optical paths is zero or an integer multiple n). Since a crystal is made up of many unit cells, constructive interference among all of them results in a strong beam enough to be measured by a detector. This technique is based on constructive interference of X-rays and satisfy Bragg's law: ($n\lambda = 2dsin\theta$)

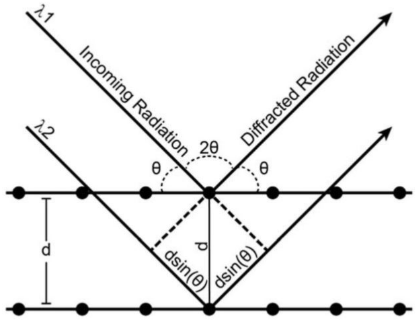


Figure 2.17: Schematic representation of Bragg's law conditions. Image extracted from: X-ray diffraction under extreme conditions at the Advanced Light Source.[34]

Which relates the wavelength (λ) to the diffraction angle (θ), and the grating spacing in a crystalline sample (d). The conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings like a fingerprint.[35]

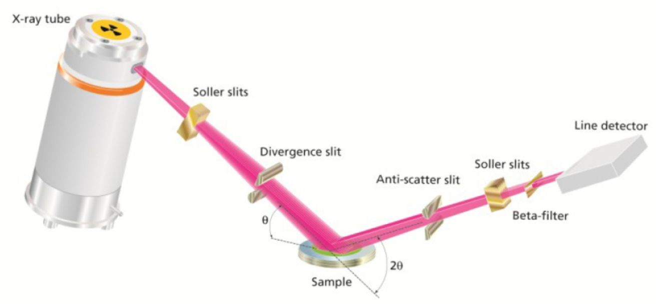


Figure 2.18: XRD basic setup. Image adapted from: Rapid X-ray diffraction (XRD) for grade control of bauxites[36]

X-ray crystallography helps us to identify unknown agents (contaminants) in carbon fibers. Also, to determine the purity of these, how will change the orientation distribution or interplanar distance of the planes depending on small changes in the manufacturing (graphitization, temperature, pressure, among other factors) of fibers. There may be a limitation in the measurement of nanomaterials, since measurements obtained by diffraction represent an average of the atomic positions for all molecules in the crystal. Because the average electron density is spread over the totality of the space that these atoms can occupy, and the disordered parts of the molecule are invisible.[35]

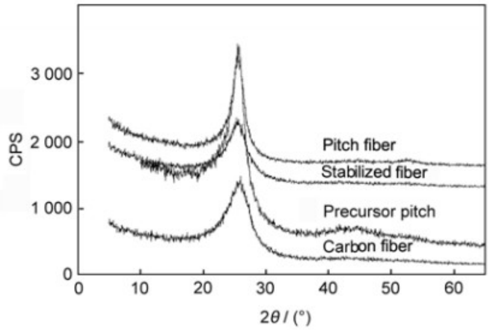


Figure 2.19: Example of XRD profiles of precursor pitch. Image extracted from: Preparation and characterization of pitch-based carbon fibers.[37]

2.4.5 Absorption Spectroscopy (UV-vis)

The Absorption Spectroscopy (UV-vis) is a photon emission spectroscopy. This method uses electromagnetic radiation (light) from the visible, ultraviolet (UV), and near infrared (NIR) regions of the electromagnetic spectrum (380 - 780 nm).[38] The absorbed radiation causes electronic transitions that can be quantified. With this technique it is possible to identify the functional groups of the molecules, in addition to quantitatively determining the components of solutions of transition metal ions and highly conjugated organic compounds. This technique involves the absorption of ultraviolet - visible radiation by the valence electrons of a molecule. Causing the promotion of an electron from a ground state to an excited state. Which leads to the release of excess energy in the form of heat.[39]

One of the following electronic transitions is required for the electron to be promoted to status:

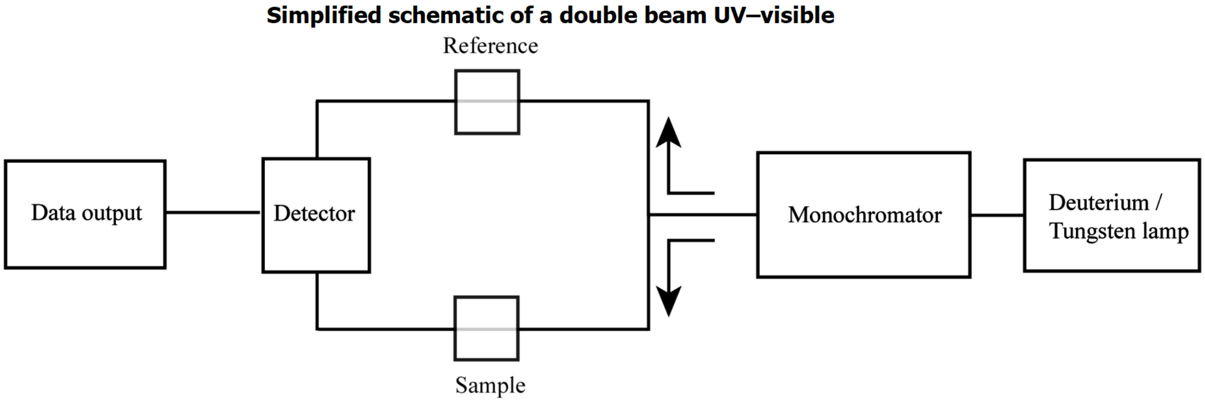


Figure 2.20: Double beam UV-vis diagram

Transition $\sigma \rightarrow \sigma^*$

This type of transitions occur mainly in hydrocarbons that only have bonds (C-H and C-C).This wavelength is around 150 nm.[39]

Transition $n \rightarrow \sigma^*$

This type of transitions correspond to hydrocarbons that have atoms with unshared pairs of electrons(no bonding electrons). This wavelength is around 150-200 nm.[39]

Transition $n \rightarrow \pi^*$ **and** $\pi \rightarrow \pi^*$

This type of transitions correspond to chromophore groups. The possible electronic transitions between n orbitals: orbital containing unshared pair of electrons. The excitation energies in the $\pi \rightarrow \pi^*$ transitions are moderately high, corresponding to the Far and Near UV region, while the $n \rightarrow \pi^*$ are considerably lower, corresponding to the visible region of the spectrum.[39]

UV-vis spectroscopy is not commonly used to characterize the fibers themselves, but it is used to characterize certain precursors or dopants that will be used in their manufacture. In this way, the size, shape, among other aspects of the compounds that will give the fibers the special characteristics, is controlled.[39]

2.4.6 X-ray Photoelectron Spectroscopy (XPS)

The X-ray Photoelectron Spectroscopy (XPS) also know as electron spectroscopy for chemical analysis (ESCA) is a surface characterization method of photoelectron spectrometry that involves the measurement of the spectra of photoelectrons induced by X-ray photons. This technique was developed in 1960 by Kai Siegbahn in Uppsala University (Sweden) and consists of irradiating a sample with a source of low-energy X-rays in an ultrahigh vacuum environment. The photoemission occurs when the frequency of the excitation X-rays is greater than the binding energy of core electrons. The photoelectrons provide us information about the energy of each level, therefore, the nature of each emitting atom. It is possible due that the core electrons possess unique binding energy, that only can correspond to a specific atom. Analyzing the peak areas and the binding energies is possible to obtain a quantitative elemental analysis. Also estimate the stoichiometry, chemical state, and electronic structure of elements that exist in a material. It is important to note that this technique can only analyze 1-2 nm depth of the sample, for this reason, it is advisable to complete with another type of analysis.[40]

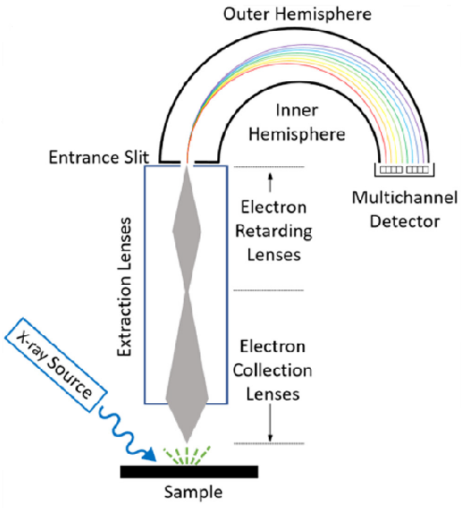


Figure 2.21: XPS basic setup. Image adapted from: Introduction to x-ray photoelectron spectroscopy[41]

This is a technique that allows us to analyze the surface of carbon fibers. It can give us information about the chemical composition as well as its chemical bonds. This technique can provide us with information about the role of the surface treatment of these. An example of these measurements is show in Figure 2.22 can be observed the narrow spectra of that the carbon fiber treated with ($O_2(O_2 + N_2)$). The peak region be deconvoluted into three functional components how is show in the figure. It has a 69% improvement corresponding to the carbonyl groups. It is shown with an increase in the counts in the analysis.[42]

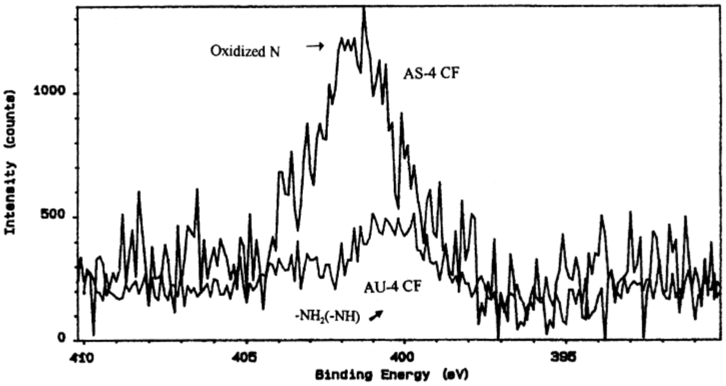


Figure 2.22: Example of a narrow scan spectra of a carbon fiber AU-4 (Non-treated) and a surface treated carbon fiber AS-4 (Treated). Image extracted from: XPS study of carbon fiber surfaces treated by thermal oxidation in a gas mixture of $O_2(O_2 + N_2)$[42]

2.4.7 Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) is a non-destructive high-resolution microscope capable of images of the surface of a sample using electron-matter interactions. This microscope was developed in the 1960s in the laboratory of Charles William Oatley, at the University of Cambridge. The principle of operation of this microscope consists in accelerating electrons in an electric field, in order to take advantage of their wave behavior. When the electrons hit the sample, interactions occur at various depths between the electrons and the atoms in the sample. The energy that electrons lose (kinetic energy) when they "collide" with the sample can cause other electrons to fly off (secondary electrons), producing X-rays, back-scattered electrons, photons, visible light, and heat.[43]

Although back-scattered electrons and secondary electrons are commonly used to image samples, each does its job. The back-scattered electrons are used to illustrate compositional contrasts in samples. Secondary electrons are used to show morphology and topography in the samples.[43]

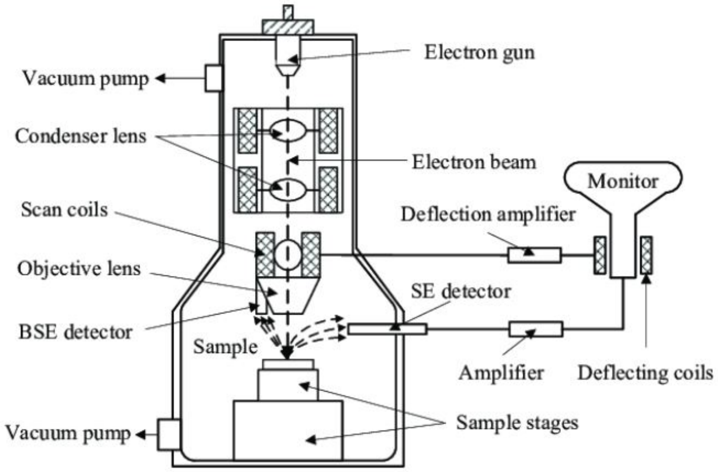


Figure 2.23: SEM basic setup. Image extracted from: A Review of Computer Microvision-Based Precision Motion Measurement: Principles, Characteristics, and Applications[44]

Scanning Electron Microscopy (SEM) is used to take high-resolution images of surface carbon fibers. It can bring us 0.4 - 20 nm of resolution. The analysis of carbon fibers with its technique can show the surface texture (if it is: smooth or rough) or morphological structure like fractures or observe the texture of sides. One problem with this technique is that the sample needs to be conductive, which is why in the vast majority of cases the carbon fibers need to be coated.[31] This technique offers only black and white images since they do not use visible light, also a great advantage is that with different methods such as: Photogrammetry and Stereophotography, 3D images can be obtained.[43]

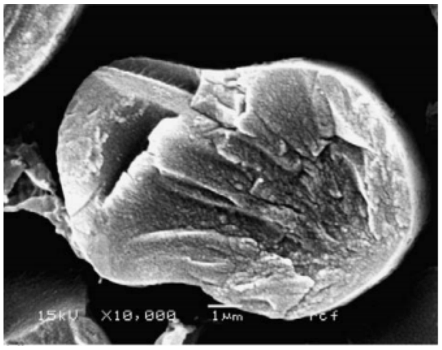


Figure 2.24: Example of SEM image of the surface and cross-section morphology of rayon carbon fiber. Image extracted from: SEM/STM studies on the surface structure of a novel carbon fiber from lyocell[31]

2.5 Carbon Materials

2.5.1 Carbon Nanotubes

They are tubes made of carbon with diameters normally measured in nanometers. These Carbon Nanotubes can be single-walled (SWCNT) or multi-walled (MWCNT) (two or more walls). This material can exhibit excellent electrical conductivity, tensile strength, and thermal conductivity. It is due to their nanostructure and bond strength between its carbon atoms.[45]

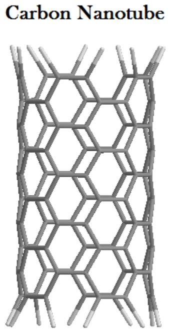


Figure 2.25: Simple Wall Carbon Nanotube

The single-walled (SWCNT) has a hexagonal lattice with a cylindrical shape. Its physical properties can vary depending on the orientation of hexagonal carbon rings. This configuration can be armchair or zigzag (Fig 2.25).[46] The multi-walled (MWCNT) has a higher probability of defects due to its large number of walls, which results in lower performance. they are easy to produce and purify, which leads to a lower cost of production. They are also mostly functionalized, due to the fact that their mechanical and electrical properties are modified when some double bonds (C = C) will break, leaving "holes" in the nanotube structure and changing their properties.[46]

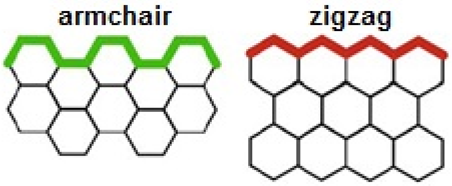


Figure 2.26: Orientation of CNTs. Figure extracted from: Mechanics of Carbon Nanotubes: Fundamentals, Modeling and Safety[46]

Its large molecular mass gives it unique physical properties including hardness, high elasticity, viscoelasticity, and a tendency to form amorphous and/or semi-crystalline structures rather than crystals.[47]

2.6 Carbon fibers

Carbon fibers are a very strong and lightweight material, usually, the fibers are not used as such, but are doped to alter their properties. They contain at least 92 *wt%* carbon, if the containing is higher they are considered Graphite fiber. They are synthetic fibers based on carbon with filaments between 5 and 10 micrometers in diameter. carbon fibers differ from graphite because they are amorphous, which gives them excellent physical and chemical properties such as high thermal and chemical stability. This also gives it a low density and good thermal and electrical conductivity.[48]

carbon fibers were developed for the space industry and subsequently applied to different fields such as: aeronautics, automobile, and boats. Among other common articles there are sport equipment, musical instruments, prosthesis, construction of molding and compounding where the mechanical properties of carbon fibers stand out.[1]

2.6.1 Carbon fibers properties

The properties of carbon fibers start from their atomic structure. Its structure is similar to a graphite or graphene, where it consists of a regular hexagonal pattern arrangement of carbon atoms layers. The properties of carbon fiber will depend on the type of fiber. It can change from it precursor (PAM, MP, or cellulosic), manufacturing process, and also if it is doped.[48]

Depending on the manufacturing we can have turbostatic, graphitic or hybrid structure. A graphitic structure can be observed in the most of the cases when the precursor is mesophase pitch Mesophase pitch (MP), and the turbostatic structure when the precursor is PAM. In the **Graphitic crystalline regions**, the layers are stacked parallel to another in a regular fashion. The atoms in the plane have SP2 hybridization. In the **Turbostatic structure**, graphene sheets are stacked irregularly (random), where they can be tilted, bent or split.[48]

Xiasong Huang (2009) proposes that microstructure affects fiber properties. This means that the strength of the fiber can be altered by increasing or decreasing the size of the reinforcing elements, in addition to changing the stress concentration of the fiber (braiding). As the fibers contain a high amount of delocalized electrons π and also the graphene layers are aligned parallel along the fiber, they present good thermal and electrical conductivity. The mesophase pitch carbon fibers or (MP carbon fiber) has a higher electric conductivity than Polyacrylonitrile (PAN) carbon fibers.[48]

Due to the fibers have a high crystallinity it presents a negative and small coefficient of linear thermal expansion Coefficient of linear thermal expansion (CLTE). Furthermore, it has been shown that when the Young's modulus increases in the direction of the fiber, the absolute value of CLTE increases.[48]

2.7 Carbon fiber's Synthesis

For a better understanding of carbon fibers, their properties, and behavior, we must begin to analyze them from their precursors. So we can understand how its manufacturing method (top down or bottom up), precursors, or whether functionalized can influence their properties, efficiency, and cost of production.[48]

2.7.1 Precursors

The principal precursors used in carbon fiber fabrication are MP, PAN, cellulosic precursors, and other form precursors. Many other precursors have been used in carbon fiber fabrication, but they are not enough important in production due to their lack of certain properties or difficulty in manufacturing. Ideal precursors have the characteristics that they are easy to convert into carbon fibers, cost-effective, and high yield.[1]

Acrylic Precursors

Various Acrylic precursors are utilized to produce carbon fibers. The majority of fibers produced with Acrylic precursors are manufactured with pyrolisis. The principal acrylic precursor is PAN for its characteristic properties.[1]

1. PAN precursors

   We can classify PAN-based polymers precursors in homopolymers and comonomers. The homopolymers has a very difficult way due to its initial oxidation state that is very difficult to control. For this reason, the comonomers are widely used and homopolymers generally never used for manufacturing carbon fibers. The comonomers exert an effect on the stabilization process, enhancing the segmental mobility of the chain, and resulting in better mechanical properties.[49] There are some comonomers like Acids, vinyl esters, vinyl amides, vinyl halide, ammonium salts, and sodium salts. But the more effective comonomers are itaconic acid > methacrylic acid > acrylic acid > acrylamide for acrylonitrile.[1]

   The acrylonitrile is used in the production of polyacrylonitrile resin (C_3H_3N), through a polymerization process, it is explained in the manufacturing PAM process.

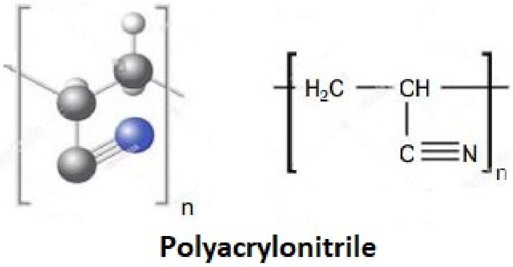


Figure 2.27: Chemical structure of polyacrylonitrile. Image extracted from: carbon fiber 2nd Edition, Chapter 2 - Raw materials and processes for the production of carbon fiber[49]

Cellulosic Precursors

The cellulosic precursor was one of the first precursors used in the manufacture of carbon fibers. The cellulose through the pyrolysis form strong carbon bonds. The advantages of cellulosic precursors are low cost, mechanical flexibility, high purity, and high thermal conductivity. Although the properties of this kind of fibers were not the most optimal (inter filament de-bonding, large void content, and low carbon yield). For this reason, they were later improved by postcarbonization treatment. However, this procedure was not applied immediately due to its high production cost. Over the years, new methods were discovered to convert cellulose to carbon more efficiently.[50]

1. Rayon Precursors

   We have some types of rayon, such as Viscose rayon, Cuprammonium rayon, and saponified cellulose acetate rayon. These precursors are used to form cellulose.[50]

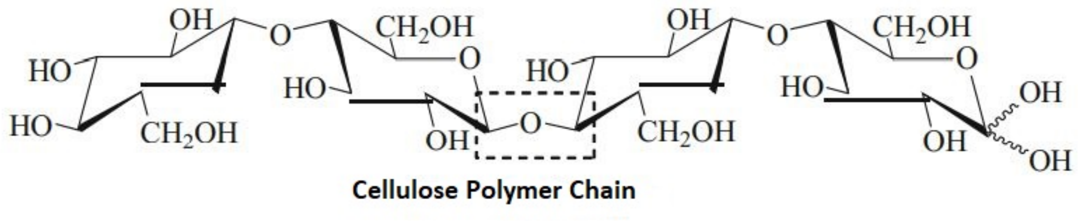
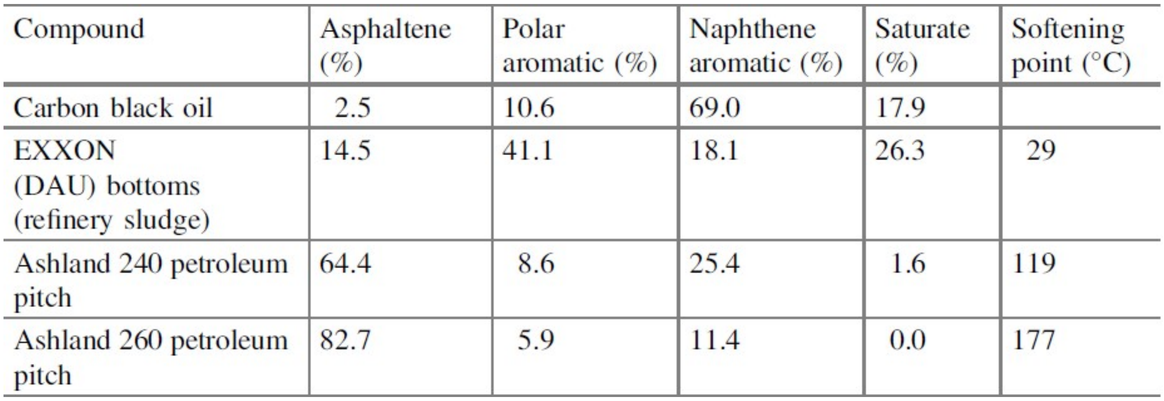


Figure 2.28: Cellulose polymer chain. Image extracted from: carbon fibers Second edition[1]

Pitch Precursors

Pitch precursors are blends of heterocyclic compounds and polyarmonic molecules, which are used like carbon fiber precursors. These precursors contain more than 80% of carbon. The pitches can be obtained from: Pyrolysis of PVC, Natural asphalt, destructive distillation of coal, and petroleum refining.[1] We can have natural and synthetic pitches; the more common ones are petroleum pitch and coil pitch. The pitch precursors have four mainly components: Asphaltenes, Polar aromatics, Naphthene Aromatics, and Saturates (aliphatic compounds).[37] The production of pitch carbon fibers is expensive in comparison with pan carbon fibers. But generally has better thermal and electrical properties.[49]

In the Fig 2.29 can be observed some commons oils and pitches, and their compositions.



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

Figure 2.29: Composition of various oils and Pitches. Image extracted from: Precursors and Manufacturing of carbon fibers[1]

1. Petroleum Pitch Precursors

   Petroleum Pitch Precursors can be obtained from residues of crude oil distillations, gas oils, catalytic cracking process, among others. Many methods can be used for the production of pitch and are based on an initial refining process, some of these methods are distillation, air bowing, prolonged heat treatment, steam stripping and low vacuum.[49]

   The Physical and Chemical characteristics of petroleum pitch depend on conditions and process employed, like time (heat-treatment time) and temperature. The higher temperatures and longer times in manufacturing produce an increased aromaticity and anisotropic contents, although petroleum pitches are less aromatic than Coal-Tar pitches.[1]

2. Coal-Tar Pitch Precursors

   Coal-Tar Pitch Precursors can be obtained from bituminous products (Coal tar) using a heat-treatment or distillation process. The pitch corresponds to the residue from the removal of heavy oil fractions. The pitches are mixtures of different organic compounds. The properties and compositions can vary from the source of tar and methods used. The majority of these compounds are aromatic (contain one or more rings with pi electrons delocalized), and the rest are heterocyclic (cyclic compound that has atoms of at least two different elements as members of its ring).[1]

Other Form Precursors

Many polymers can be used like carbon fiber precursor. Among these are natural fibers such as: chitosan, silk, eucalyptus, among others. Many of them can be used like carbon fiber precursors with similar or less cost production, but they do not have good mechanical properties. Linear polymers precursors require heat stretching to obtain high performance, and even in this way have a low carbon content. Aromatic polymers precursors have a high carbon yield and are stables. Aromatic polymers precursors have a high carbon yield and are stable, but they have a high-cost production and cannot have high performance.[1]

2.7.2 Manufacturing Methods of carbon fibers

The manufacturing methods are one of the main reasons why carbon fibers change their mechanical properties. This section will analyze the methods of manufacturing the precursors mentioned above.

From PAN-Based Precursors

The carbon fibers based on PAN-Based precursors are optimum because of its tensile and compressive properties as well as the carbon concentration. The manufacturing steps could be categorized in: Polymerization, spinning fibers, thermal stabilization, carbonization, graphitization, and surface treatment. The majority of times PAN-Based copolymers precursors are used, these contain acids like: methacrylic acid, acrylic acid, itaconic acid, and mathacrylate acid that affect the stabilization and the molecular alignment.[1] The steps for manufacturing carbon fibers from PAN-Based precursors are described below:

1. Polymerization and spinning

   First, need to be produced the PAM-based precursor through polymerization methods. For this is generally used acrylonitrile and comonomers. The polymerization methods are solution polymerization, emulsion polymerization, bulk polymerization, and aqueous dispersion polymerization. All of these methods consist of chemically grouping monomers and acrylonitrile, giving rise to a molecule of greater weight (polymer).[51] The PAN polymer precursor (polyacrylonitrile) is the backbone of the chemical structure of the fibers, and these precursors generally contain polar nitrile groups (R-C≡N). The spinning consists of the extrusion of the polymers that use a spinneret to form multiple continuous filaments. The wet spinning is the most used method of producing commercial carbon fibers due to it low cost and efficiency.[49]

2. Thermal stabilization

   The thermal stabilization is a very important step where the fiber characteristics are controlled. It is important to establish proper conditions for optimum stabilization of the precursors conditions such as temperature, time, and heating rate. The fibber is stabilized by controlled low temperature between 200-300 Celsius degrees. The process consists in converting the linear molecules of PAN-Based polymer into cyclic structures.[52]

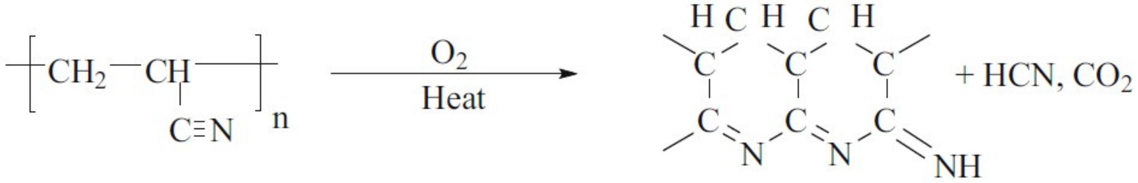


Figure 2.30: Example of Mechanism of cyclization. Image extracted from: Precursors and Manufacturing of carbon fibers[1]

3. Graphitization and Carbonization

   The carbonization is the conversion of organic materials into carbon. The Carbonization and Graphitization are carried out in an atmosphere controlled with Argon (Ar_2) or Nitrogen (N_2). Argon gas provides better mechanical properties, but it is more expensive than nitrogen. The temperature used in the carbonization determines the application of carbon fibers. Between the temperatures of 1500-1600 $^{\circ}C$ is used for high-strength applications, above these temperatures a decrease in tensile strength occurs. To perform the graphitization is required other heat treatment above 1800 $^{\circ}C$ and up to 3000 $^{\circ}C$ needed to obtain a high modulus in fibers. It is important to consider that Nitrogen (N_2) cannot be used in temperatures above 2000 $^{\circ}C$ owing to its reaction with carbon to form cyanogen.[52]

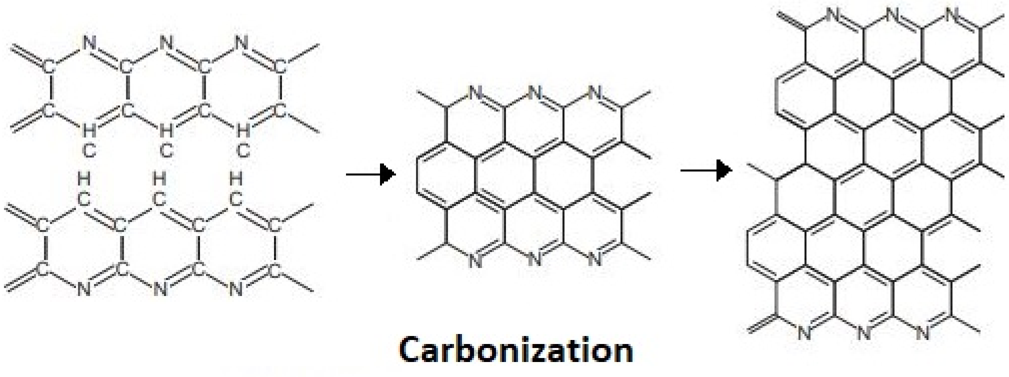


Figure 2.31: PAM carbonization process. Image extracted from: carbon fiber 2nd Edition[49]

4. Surface treatment

   The surface treatment consists of an alteration of the surface of fibers, and it is used to improve the mechanical properties of carbon fibers. The surface-treatment process could be categorized as liquid and gaseous oxidation treatments. The anodic oxidation belongs to the liquid type method, and it is widely used due to its low cost, efficiency, and time. After the surface treatment is necessary to clean the excess electrolyte with a huge amount of water (water baths).[52]

5. Drying, preparation (sizing), and winding

   This part of the process is one of the most important steps. First, is needed that the carbon fibers can be protected or/and lubricated to avoid their brittleness. Sizing requires materials that are compatible with the matrix resin (solubility and reactivity) for no change in the chemical or physical characteristics during storage. Generally these materials are emulsifiers and resins. The epoxy resins are more used and need to be controlled carefully to obtain the properties required. After the sizing, the fibers are dried and collected using winders.[52]

From Cellulosic precursors

Rayon fibers can be converted into carbon fibers with physical, chemical, microstructural, and mechanical changes through carbonization and stabilization process. In this section, processes like stabilization, carbonization, and graphitization for manufacturing cellulosic carbon fibers were described. The process of surface treatment, sizing, and winding is the same to the PAN-Based carbon fibers.[1]

1. Stabilization

   The cellulose is a linear polymer, glucose-based, it has glycosidic linkages. The hydroxyl groups form hydrogen bonds, and their bonds lead to crystalline arrangements. In theory, this type of fiber has a yield of 44.4% of carbon, nevertheless, the actual yield corresponds between 10 - 30 % of carbon. This yield comes from the depolymerization of macromolecular chains and subsequently the elimination of carbon in the forms of aldehydes, carbon monoxide (CO), organic acid, and carbon dioxide ($C0_2$).[1]

   The cellulose degradation begins in an atmosphere controlled with low temperature, its thermal stability depends on the process conditions. This complex process produces a variety of oxygenated compounds, which leads to a significant loss of carbon yield. There are two methods to prevent it, the modification of cellulose precursor and the pyrolysis of the cellulose.[1]

2. Carbonization

   The carbonization of cellulose is the conversion process (through repolymerization) of depolymerized structure into graphite-like layers. To perform the Carbonization first is dehydrated with a temperature between 25 - 150 $°C$ to continue the various temperatures are applied from 300 to 900 $°C$ at an atmosphere controlled, It causes the formation of semiordered carobonaceous structures.[1]

3. Graphitization

   The graphitization is performed between the temperatures of 900 - 3000 $°C$ to obtain high modulus fibers. It is due to a change in the order of graphene stacks, both laterally between the layers and along the fiber axis. The modulus of Young is increased by increasing the heat treatment. Applying tension in this process, we can obtain a better content of carbon, increases the fiber density resulting from the growth of crystallines.[1]

From Pitch-Based Precursors

The carbon fibers from pitch-based precursors are manufactured in several steps: precursors production, stabilization of precursors, carbonization, and graphitization. In this kind of fiber, the stabilization process is the most important because in this stage the thermal oxidation occurs in the precursor fiber. The process of surface treatment, sizing, and winding at the same to the PAN-Based carbon fibers.[53]

1. Production of precursors

   The production of the precursor is carried out by melt spinning. The melt spinning consists of three steps: melting the precursor, extrusion (by spinning capillarity), and drawing as they cool. This process forms the structure in the mesophase pitch-based fiber, and the thermal treatments reinforce the structure.[1] Many factors intervene in the development of ordered graphitic structures. The first is the melt temperature because each mesophase has its own melt temperature where spinning is possible. Spinning below these ranges produces fibers with high viscosity and fractures in drawdown. Temperatures above these ranges produce thermal degradation and low viscosity. Therefore, low viscosity is necessary to produce good quality carbon fibers.[49]

2. Stabilization of precursors

   The pitch based precursors are similar to PAN precursor fibers, it can not be treated at high temperatures due are infusible or oxidized in these conditions. The oxidation temperature is below the fiber softening point to maintain the orientation of the structure. The oxidized molecules contain carboxyl, carbonyl, and ketone groups, which allow stronger hydrogen bonding. The introduction of oxygen and this hydrogen bond helps the three-dimensional cross-linking. Some solutions like methanol or iodine are used to improve the stabilization time or increase the carbon yield.[1]

3. Carbonization and graphitization

   Once the fibers are stabilized, we proceed to carbonization and graphitization. The fibers were precarbonized in order to prevent or avoid the defects produced by the release of volatiles. Then the carbon fibers are produced, carbonizing the stabilized fibers. To perform the graphitization necessary to use temperatures close to 3000 Celsius degrees to improve Young's modulus and the alignment of the crystalline.[1]

   The orientation of the layers influences the orientation of the final carbon fiber. So the graphite layers are ordered along the fiber axis, but transverse structures are oriented according to velocity gradients (radially, circumferentially, and randomly). Then, adjusting the microstructure in the precursor, the carbon fiber strength could be improved. Changing the flow properties in the melt spinning could modify the microstructure.[1]

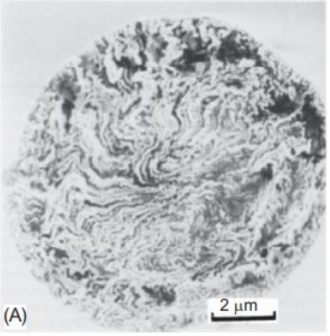


Figure 2.32: Example of Scanning electron micrographs of pitch carbon fibers. Image extracted from: carbon fiber 2nd Edition[49]

It is important to consider that some companies to improve the tensile strength use agitation in the spinneret, it produces a random distribution for the folded graphene layers. Another way to change the microstructure is by changing the spinning temperature.[53]

Chapter 3

Discussion and bibliographic analysis

In the last sections the history of nanomaterials was analyzed, their evolution until the appearance of carbon fibers. The production process of these was also analyzed in detail, taking into account their precursors, properties, and behavior. Subsequently, the research methodology for the thesis was analyzed and described. In this section, the advantages or disadvantages of carbon fibers depending on their precursors and manufacturing were analyzed. How these improve their mechanical properties with small changes in their process. In this way, they are able to adapt to different needs of the consumer.

In carbon fiber manufacturing, the principal considerable variable is the precursor, but it was analyzed in the past sections. The carbon fibers can also be classified in other variables like their tensile strength, modulus strength, or braided. Considering the modulus strength, the fibers can be classified in High strength (HT) (HT with >4 GPa), Low modulus strength (LM) (LM with >100 GPa), Intermediate modulus (IM) (IM with >200 GPa), High modulus (HG) (HG with >300 GPa), and Ultra-high modulus (UHM) (UHM with >500 GPa).

At the moment of characterizing carbon fibers, it is very important to take into account what each technique offers us, what are its advantages and disadvantages. Washer and Blum found that with Raman characterization of carbon fibers using 752 nm incident laser. It was possible to observe that it is a non-destructive technique where it was found that from pitch carbon fibers four bands were observed D, G, D', and G' while from PAN- carbon fibers only D and G bands were present. It can be observed in figure 3.1. Also was demonstrated that the bands D and G present strain dependence (change bands values in dependence of their tensile strain). If the tensile strain increases, the resonance frequency decreases. These indicate that Raman spectroscopy is ideal to make strain measurements in carbon fibers.[28]

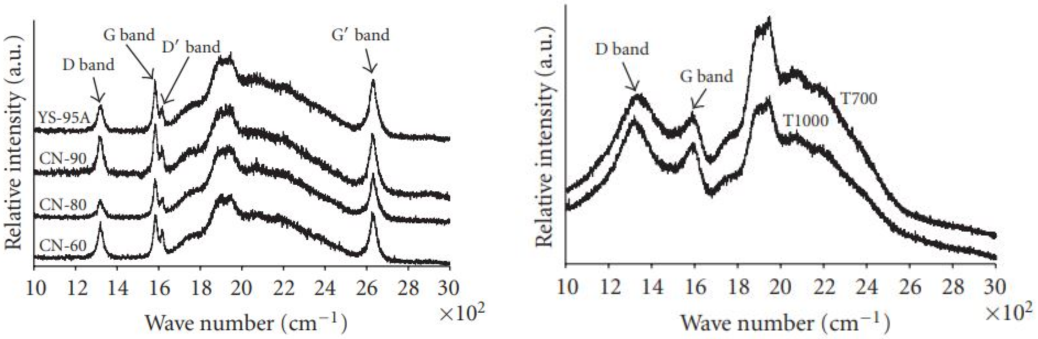


Figure 3.1: Raman bands for pitch- and PAN-carbon fibers. Images extracted from: Raman Spectroscopy for the Nondestructive Testing of Carbon Fiber.[28]

Although the method of obtaining and characteristics of cellulose carbon fibers was already analyzed in the previous section, there are certain compounds such as lyocell with which its manufacture is interesting. The lyocell is extracted from eucalyptus wood, although it is also common to find Lyocell made of oak, bamboo and birch. This is broken down into pieces and then chemicals are added to dissolve it in a wood pulp. Wu investigate and compare the lyocell carbon fibers (LCF) and rayon carbon fibers (RCF) through scanning tunneling microscopy (STM) and scanning electron microscopy (SEM).[31]

The SEM characterization shows that a rougher surface with grooves and cracks for RCF, while a smoother surface for LCF. It can be appreciated in Figure 3.2. Wu states that this is one of the reasons for the decrease in tensile strength for RCF. There is a small difference of strengths between RCF and LCF, although the single-strand strength of lyocell is twice higher than that of rayon.[31]

With the STM analysis at (500 nm × 500 nm) magnification that the surfaces of LCF are characterized by bulk structure. Also, can be observed smaller slug-like microstructures of 25 - 150 nm of length, aligned with an angle of 45° to the axis. Due to the bulk structure and slug-like microstructure can be attributed the smoother surface of LCF. Also, can be observed that the

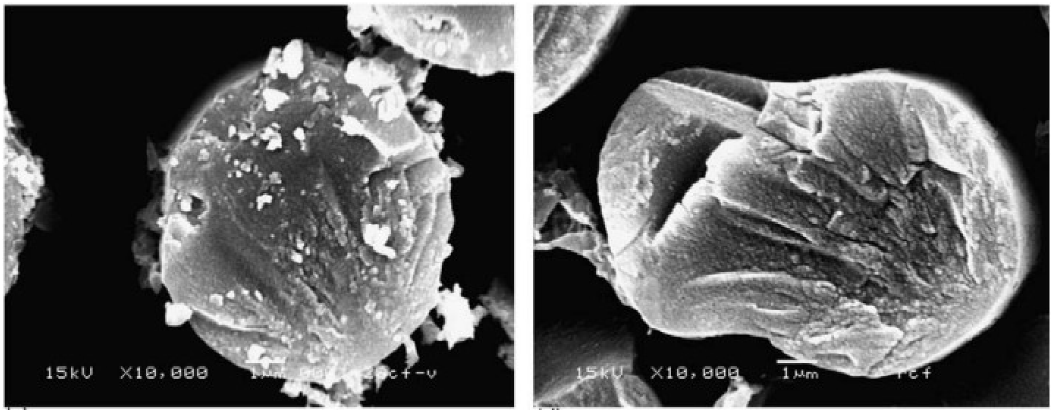


Figure 3.2: SEM image of the cross-section morphology of LCF (left) and RCF (right). Image extracted from: SEM/STM studies on the surface structure of a novel carbon fiber from lyocell[31]

slug-like microstructures stack to form the bulk structure. Incrementing the magnification to (2 nm × 2 nm) carbon atoms like brightest points are observed. The regular hexagonal rings can't be observed in LCF, this may be due to the heat-treatment temperatures, they strongly affect the structure formation of carbon fibers. It's known that a higher carbonization temperature carries a higher graphite degree, which presents larger carbon network size. So the low heat-treatment temperatures are the reason for the non-formation of hexagonal carbon rings on the surface. Furthermore, the low temperature can lead to low crystallinity and plane defects such as hetero-atoms that are not completely eliminated. This may be one reason why RCF has almost the same strength as LCF.[31]

Other compound of interest in manufacture is Lignin, Kubo suggest a potential production of carbon fibers from lignin-based fibers and synthetic plastic, specifically, the effect of blending recyclable (polypropylene) PP and (polyethylene terephthalate) PET with lignin. For the manufacturing process, both systems were spun in fibers and before the carbonization process, a stabilization process was used to avoid the fusion of individual fibers. Carbon yield decreases with the increase of synthetic plastic. However, the carbon yield increases in plastic blend fiber (25%) than common pitch carbon fiber.[54] The blend composition affects the surface morphology in both cases. The ligin-PP fibers resulted in a hollow and/or porous carbon fiber, while lignin–PET fibers have a smooth surface. In the same way, were affected the mechanical properties of carbon fibers.[54]

The analysis of the precursor fibers shows that lignin/PP blends are immiscible, while lignin/PET blends are miscible. A problem shown is that only the PP with a specific viscosity was able to be continuously spun into fibers. Another problem occurs in the thermostabilization process due to the polymer blending with PET and PP. The lignin homofibers required slow heating rates. It is due, higher heating rates resulting in the fibers fusing together.[54]

The optimal ratio of lignin/synthetic polymer were 75:25 w/w. Synthetic polymer blending affected the mechanical properties of the fibers. The material produce in this research work is slightly better than reported for commercial carbon fibers. The carbon fibers prepared from the immiscible lignin/PP fibers were porous, while miscible lignin/PET blends fiber had smooth surfaces.[54]

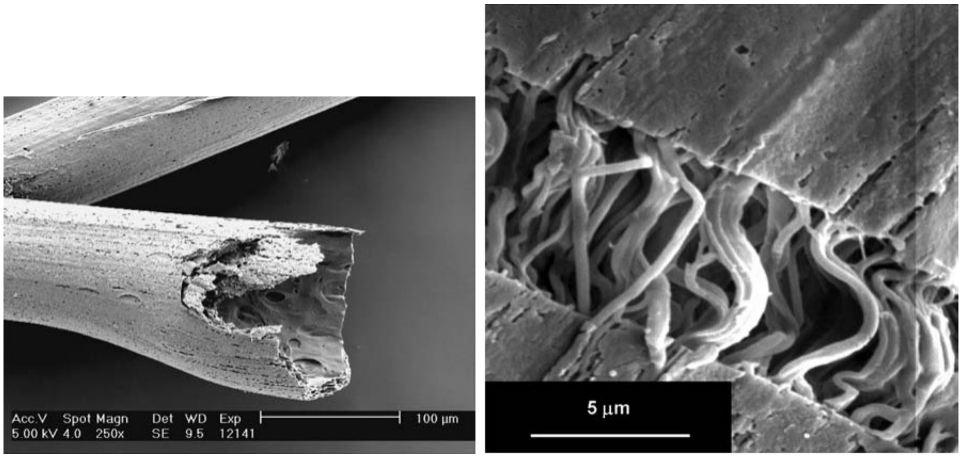


Figure 3.3: SEM analysis of lignin/PP blend carbon fibers at different magnification. Image extracted from: Lignin-based Carbon Fibers: Effect of Synthetic Polymer Blending on Fiber Properties[54]

In Figure 3.3. is possible to appreciate the poly(propylene) phase spread all over the lignin phase at a magnification of 100 μm and the point of fracture at 5 μm. In the SEM images is showed various kinds of pores on the cross-section and surface. These pores were produced from melting out of lignin/PP fiber prior to pyrolysis.[54]

Graphene-doped carbon fibers were analyzed, also Zhen Xu and Chao Gao showed that fibers can be made by using graphite or Carbon Nanotubes (CNTs) as a precursor. The graphene has excellent properties that provide to the carbon fibers mechanical properties. Structurally in the atomic to micro scale the Graphene Fibers (GFs) are made of aligned graphene sheets while common carbon fibers are made of nano-graphite crystals interconnected.[55]

Also, the crystal graphene sheets size is larger than nano-graphite crystals corresponding to the Carbon Fibers (CFs), it can provide some superior properties controlled by grain boundaries of GFs compared to CFs. The principal issue of these fibers is that to upgrade their combined performance electrical/thermal conductivities and mechanical strength. It is needed improving the mechanical properties, a more compact microstructure and regular alignment can be achieved by optimizing the spinning parameters. To improve electrical/thermal conductivities can be optimized alignment degree of graphene.[55]

In the Figure 3.4 can be appreciated a XRD image from microstructural attributes of GF where the graphene sheets are well aligned along the fiber axis. (b) correspond to the GF surface, in it can be observed wrinkles from the shrinkage in the drying. (c) correspond to the lamellar structure of graphene-assembled. (d) correspond to the lamellar graphene sheets at the fracture tips.[55]

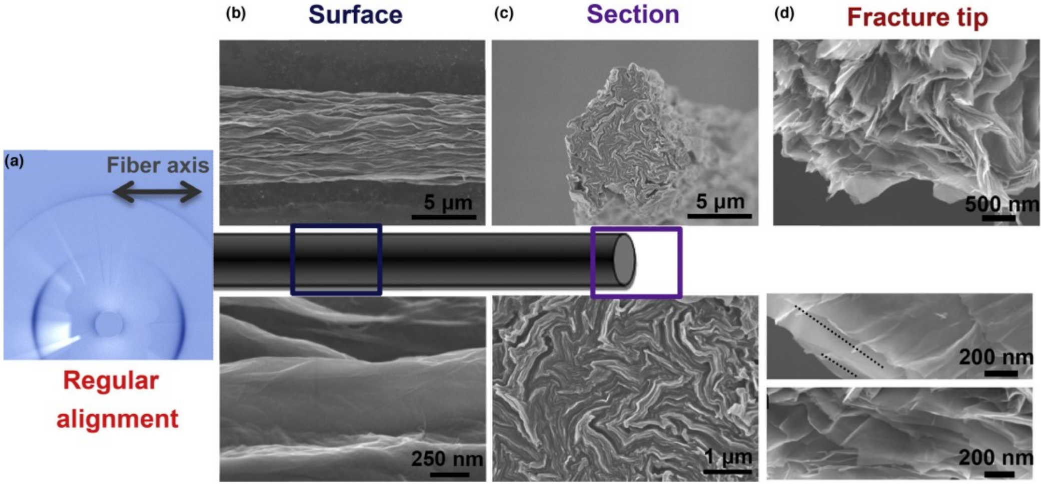


Figure 3.4: Microstructural attributes of GF. graphene sheets are well-aligned along the fiber axis. Image extracted from "graphene fiber: a new trend in carbon fibers"[55]

The first fibers that proceed with this method have good flexibility and low tensile strength

(140 MPa approx with 5.8 wt %). Given this great difference in mechanical properties, processes have been invented to improve their characteristics. There are three principal strategies to upgrade them. They consist of decreasing the structural defects (sheet boundary, impurities, voids), the alignment of graphene sheets needs to be suitable, and improve the interaction of constituent through covalent bonds. Whit this advice the tensile strength reaches 0.5 GPa. Recent advances through the use of combined methods have achieved a tensile strength of 1.1-1.2 GPa.[55]

In the electronic performance, the use of different compounds like alkali bases, HI, or HBr in the coagulation baths enhances the conductivity (at least $4.1x10^4 S/m$). If is used molecular doping mixing with other metals like gold, silver, or copper the conductivity can reach $4.1x10^4$ S/m.[55]

It is known that small changes in manufacture achieve a big change in the product resulting. The classic way to manufacture the PAN is with wet spinning, but recent breakthroughs show that using gel spinning, is obtained a higher tensile modulus. It is due to higher draw ratios. Chae demonstrated the enhanced properties with Gel spinning in his research entitled "High strength and high modulus carbon fibers" like carbon fibers gel spun polyacrylonitrile copolymer of Georgia Tech (GT) has one of the biggest values of tensile strength (5.5 -5.8 GPa) and tensile modulus (354 -375 GPa) for continuous carbonization line. In a short gauge length where he obtains tensile strength values higher than 12.1 GPa and random flaws of about 2 nm size, which leads to a tensile strength of 20 GPa.[56]

Normally, if the carbon fiber tensile modulus is increased, a decrease in tensile strength. The oxygen diffusion stabilizes the fiber structure. Due to it, the fiber cross-section is circular results in a homogeneous structure providing better tensile properties than non-homogeneous structure. Also, it can reduce the defects in the polymer chain end and chain entanglements. It is due to that a lower polymer concentration is used compared with wet spinning. The defects (structural heterogeneity) govern the tensile strength of fibers, they can appear due to inhomogeneity solution, heterogeneity solution, and heterogeneity (in carbonization and graphitization).[56]

In the figure 3.5 can be observed the SEM image of carbon fiber cross-section of an amorphous and circular structure. Where b correspond to GT PAN based carbon fibers and e correspond T1000 carbon fibers.

Carbon nanotubes are another great material that can be applied to carbon fibers. Thostenson

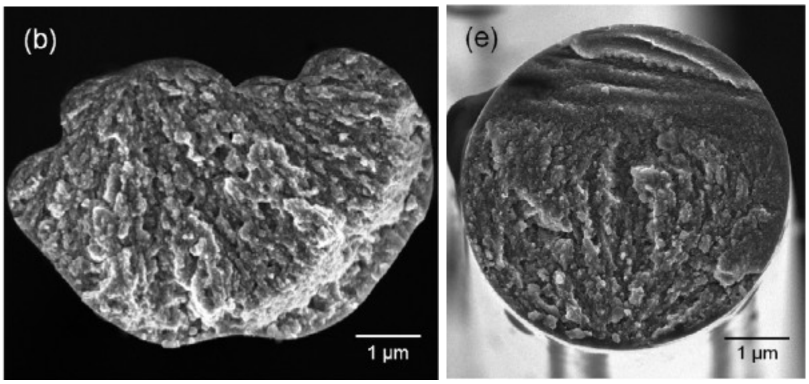


Figure 3.5: SEM image of carbon fiber cross-section of an amorphous and circular structure. Image extracted from "High strength and high modulus carbon fibers"[56]

shows that using chemical vapor deposition to grow directly carbon nanotubes is a very useful way to improve the mechanical properties of carbon fibers. When the CNTs embedded in a polymer matrix, they change in the length relative to carbon fibers, which results in a multiscale composite. Where the CNTs looks like a sheath of nanocomposite reinforcement.[57]

Thostenson examines the influence of local nanotube reinforcement on load transfer between the fiber-matrix interface. The growing of CNTs on the fiber surface result in the strongest interface. A problem shown in the manufacture is the catalyst layer not always be deposited uniformly on the surface. As a result of this, there are local areas on the fiber where amorphous carbon is deposited instead of nanotubes. Carbon fibers reflect light due to their surfaces being relatively smooth, resulting in that carbon nanotubes producing light scattering. It can be appreciated in Figure 3.6 In this figure, it is evident that the dark areas correspond to carbon nanotubes and the bright areas correspond to bare fiber.[57]

Also, it shows that the nanocomposite reinforcement improves interfacial load transfer. The nanotubes have a selective reinforcement at the fiber-matrix interface. It results in stiffening of the polymer matrix, improving load transfer and interfacial shear strength of the composites[57]

An example is the change of the gas in the oxidation of PAN carbon fibers, where oxygen (O_2) is replaced for Sulfur dioxide (SO_2). So, in this example, let us observe that sulfur incorporated in the bridges of the chemical structure, producing a rigid structure. If a heat treatment is added (high and low temperatures) the fibers present a bigger cross-linking and carbon yield, which gives

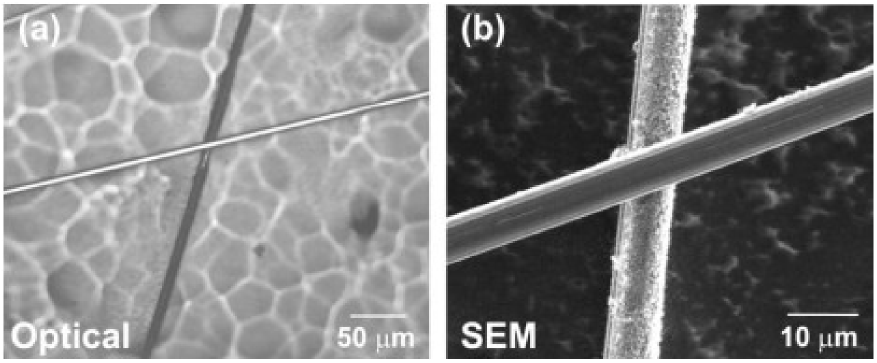


Figure 3.6: Optical (a) and electron micrograph (b) of extracted fibers from the nanotube-coated bundle. Image extracted from: Carbon nanotube/carbon fiber hybrid multiscale composites[57]

the fibers better mechanical properties.[58] Another way to improve the content in carbon yield of PAN carbon fibers performs the carbonization in chlorhydric acid (HCl) where the amount of Hydrogen cyanide (HCN) is reduced, leading a dehydration and leaving O_2 through the water. The addition of a flame retardant produces the decomposition of cellulose at a lower temperature, faster rate, and bigger carbon yield. The flame retardants also produce a faster and uniform stabilization due to better diffusion of heat.[58]

The surface treatment is a very important step in manufacturing because it provides good interlaminar shear strength, also controls the adhesion and bonding between the matrix and fiber. The process increases the surface acidic groups and the surface area, leading to good bonding between the fiber and matrix resin.[58].

Considering the morphology of carbon fibers, Chand reported that PAN carbon fibers present better tensile and compressive properties than pitch carbon fibers. It is due that PAN carbon fibers present particle-like structures and smaller crystals compared to pitch that presents shit-like structures and larger crystals. Taking into consideration the cross-section, it is proposed that pitch-based carbon fibers with a folded-radial texture present a higher compressive strength than flat-layer structure fibers. It is shown in the next figure, where the figure a. correspond to flat-layer structure and b. correspond to folded-radial structure.[58].

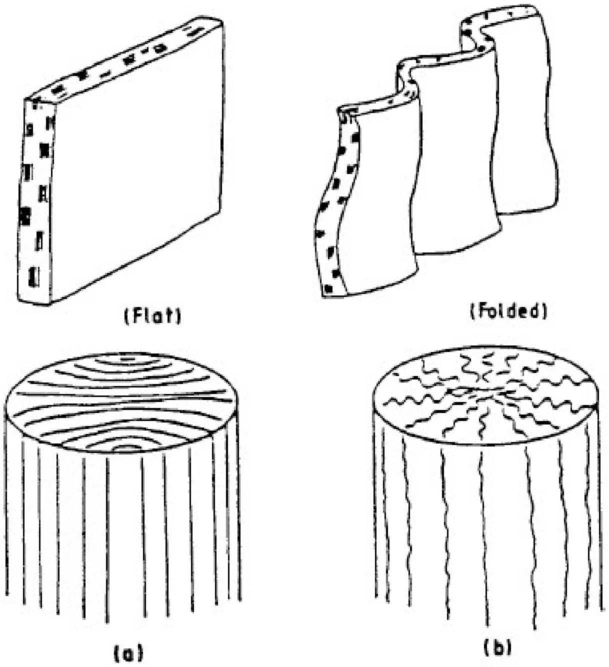


Figure 3.7: Representation of pitch-based carbon fibers with folded-radial and flat layer structure. Image extracted from "Review carbon fibers for composites"[58]

It is known that the transverse structure of carbon fibers depends on the type of spinning process, the temperature of spinning, and the shape of the spinneret. Also, it was known that compressive strength will increase if decreased the crystalline size, density, orientation, and interplanar spacing.[58]

Xuetao 2010 show in "Microstructure and ablation properties of zirconium carbide doped carbon/carbon composites" that other way in the doping of carbon fibers can be the addition of zirconium carbide (ZrC). To prepare this compound three steps are required: first is immersed in a zirconium oxychloride solution, followed by rapid densification through chemical vapor infiltration, and graphitized at 2500 C^o. It shows that linear and mass ablation is obtained. With a content of 4.14 wt % of zirconium carbide are decreased by 83 % the linear ablation and 77.0 % the mass ablation. While the carbon fiber matrix surface is glossy and smooth, the doped carbon fiber matrix surface is dim and honeycombed. Also, the formation of zirconium dioxide (ZrO_2)

leads to a decrease in bonding between the matrix and carbon fiber.[59]

With the increase in Zirconium carbide (ZrC) content, the linear ablation decrease linearly, and the mass ablation first increase but later decrease. It means that the ablation resistance increase with the Zirconium carbide (ZrC) content. The ablation mechanism is controlled by heterogeneous mass transfer.[59]

At the moment of analyzing the mechanical properties, it was observed that the compressive strength is increased when the content of ZrC is below 3.24 wt %, reaching it maximum value in 83.81 (MPa) for compressive strength and 2.91(GPa) for modulus of compression. But decrease when the content is increased to 4.14 wt %. Also, was observed that the content of carbon decrease due to the reactions with oxygen.[59]

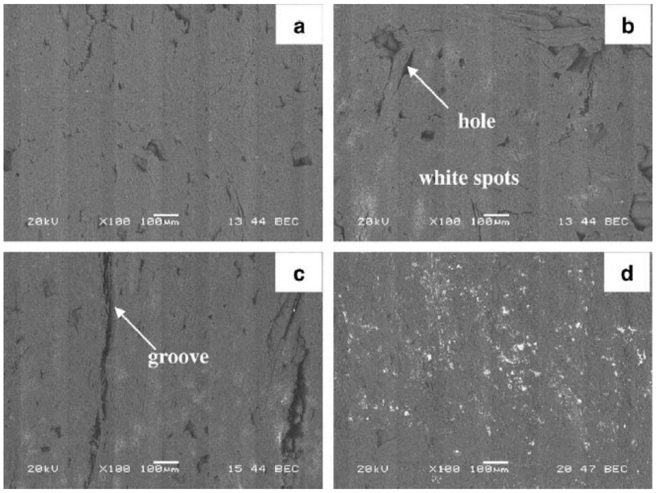


Figure 3.8: Backscatered electron images of SEM microscope. The cross section correspond to 1.19, 2.09, 2.50, and 3,24 wt. %. Image extracted from "High strength and high modulus carbon fibers"[59]

How is show in the figure 3.8 the number of defects and voids decrease with the amount of ZrC. Considering the ablation behavior the defects, pores, and interfaces between the matrix and carbon fibers are oxidized in priority. So the surface becomes perforated and loose, leading that the oxygen was provided to enter the inner substrate passages. So, when the ablation is going on are oxidized in a big way, the loose carbon matrix and carbon fiber.[59]

Considering the excellent properties (surface morphology and mechanical performance) that provide the carbon fibers, they are widely used as reinforcement in structural composite materials. Chee shows that the carbon fibers occupy the largest volume fraction of the composite and withstand most of the load. While the matrix is responsible for providing a barrier against aggressive environments, protecting the fibers from wear and abrasion damage, and keeping the fibers in place, as well as transferring tension between the fibers.[27]

The interface between the matrix and fibers has a very important role, it transfers the load from the matrix to the fibers. Which affects directly the performance of a composite (delamination and shear resistance). Considering the adhesion between the matrix and the fiber, if it is strong, the composite becomes rigid and brittle. If it is weak, the composite becomes resilient. In this way, the performance only can be maximized by improving an effective load transfer. In other words, ensuring appropriate adhesion and compatibility between the matrix and fiber. It could be achieved via suitable interactions (physical or chemical) or mechanical interlocking.[27]

The adhesion is determined from the fiber and matrix properties. There are two important factors, surface area available and roughness surface. The surface of the fiber (chemistry and energy) determines how the fiber be wetted by the matrix, and its functional groups form attractive interactions (chemical bonds). The surface area can be determined by the graphitization process, where lower temperatures produce less organized surface structure and a high ratio of micropores (increasing the surface area). While high-temperature results in a reduction of micropores (decreasing the surface area). Given this, several surface treatments are carried out to increase the surface area, such as plasma treatment, acid oxidation, and electrochemical oxidation.[27]

The wettability of carbon fibers is another important factor that determines the formation of the composite interface (matrix-fiber). Considering the surface energy, it was shown that an increase in temperature decreases the surface energy. It is due to a reduction of high-energy sites such as surface defects, usually containing highly polarizing heteroatoms. The sizing and surface treatment also decreases the surface energy. So to achieve good adhesion we need to consider chemical bonding and mechanical interlocking. It will increase the surface area and rugosity. Increasing the surface area causes that the possible favorable interactions to be increased (van der Waals and hydrogen bonding). It also leads to improved wettability of the fibers by the matrix.[27]

The carbon fibers from polypropylene (PP) are another very important case. Kumar 2002 manufactured fibers from polypropylene and polypropylene/vapor grow nano carbon fiber com-

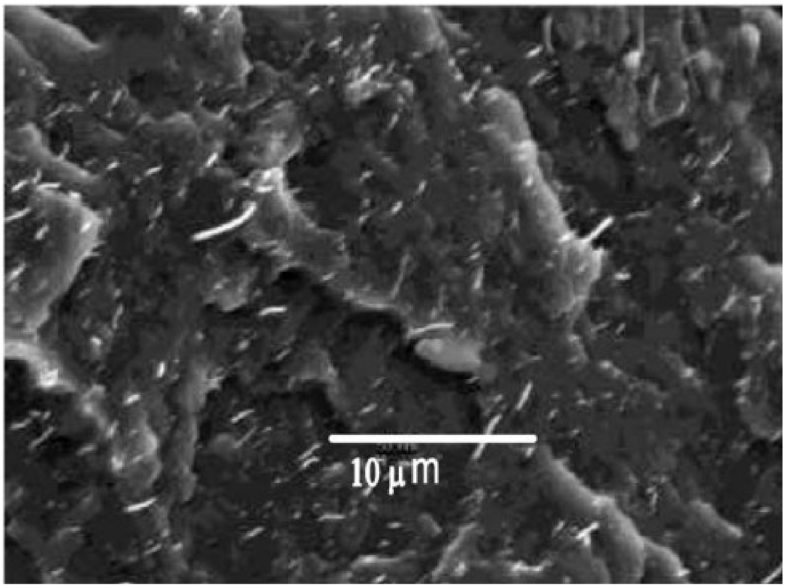


Figure 3.9: Scanning electron micrographs of fibers from PP/nano carbon fiber composite. Image extracted from: Fibers from polypropylene/nano carbon fiber composites[60]

posite using spun conventional melt spinning equipment. The vapor grow nano carbon fibers can be produced today in high volumes at low cost, and its fibers have typical diameters of (50–200) nm and lengths of (50–100) μm. Also, it knows the higher properties of CF with CNTs.[60]

It was observed that composite fibers has higher mechanical properties like modulus and compressive strength than PP control fibers, strain to failure decrease as a result of filling with the nano carbon fiber, and the tensile strength was not significantly affected. The value of the moduli of nano carbon fiber is (450 GPa) and PP fiber is (5 GPa). The composite fiber with 5 wt % has a prediction of 17 GPa. Assuming a perfect orientation for the nano fibers in the composite fiber.[60]

How can be appreciated in Figure 3.9 the SEM analysis show a good dispersion of the nano carbon fibers in the spun fibers. Also, images were taken with a confocal microscope, demonstrating that the layer close to the skin appears to have fewer nano fibers. In the layer farther away from the 'skin', the carbon nanofibers seem to be more aggregated. With an X-ray diffraction microscope, graphite (002) and polypropylene (060) reflections overlap. Suggesting a high degree of orientation for both.[60]

Activated carbon fibers (ACF) are commonly used like absorbers due to their high adsorption rates and capacities. Furthermore, their sorption and tensile strength make it the perfect material for these uses. The rayon-based activated carbon fiber (RACF) was activated directly from rayon carbon fibers (RCF) by the mixture of NaCl and H3PO4. Wang found that through AFM and SEM analysis that due to the activation process there is a decrease in the diameter from 12 to 9 μm and the grooves on surface have vanished while lots of pores emerged. It causes a big surface area, which gives it absorption properties. In the interior, the cross-section still maintains the structure of carbon fiber. It guarantees the high tensile strength of RACF.[61]

With the AFM analysis can be observed the surface becomes rough and porous, but the striations have disappeared, confirming the SEM analysis.An advantage of AMF is it can detect the depth and width of pores, as well as their distribution. There are mainly macropores and mesopores with it width between (2-50) nm.

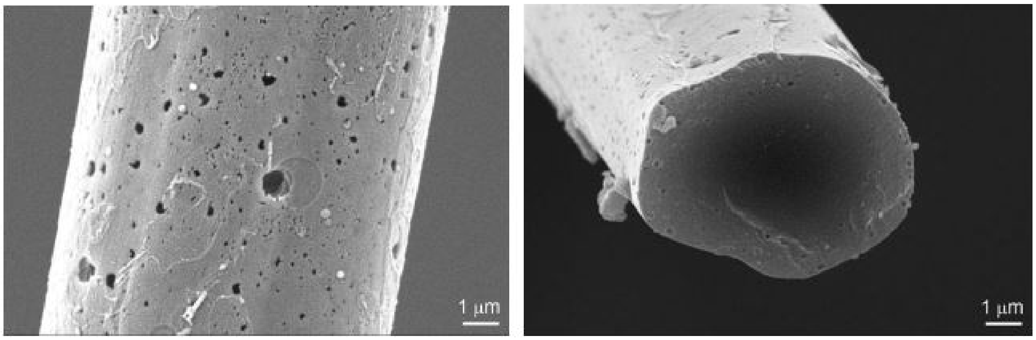


Figure 3.10: SEM images of RACF. Surface and cross-section morphology. Image extracted from: SEM and AFM studies on the surface and cross-section morphology of rayon-based activated carbon fibers.[61]

RCF exhibited striations and groove with the width ranging of (30-90) nm. The striations founded are consisted of many grains and microfibrils. In RACF many pores emerged on the superficial cross-section and surface (1-2) μm but in the interior section was close-grained. The pore sizes are in the range of (50- 500) nm. The pore walls were not smooth, they consisted of continuous grains with 30 nm of diameter.[61]

During the last decades, the use of carbon fibers has increased greatly, in the same way, the amount of waste being generated. So the treatment of waste is a becoming urgent problem.

The manufacturing waste accounts correspond to 40% of all waste, and the remaining 60 % corresponds to components and end of life. The carbon reinforcement is an expensive constituent and was shown that it is the most environmentally impacting in a composite part manufacturing. The recycling of these materials The recycling of these materials would lead to environmental and economic benefits.[62]

A solution to recover the carbon fiber reinforcement is the solvolysis of the matrix by water under supercritical conditions. It processes produces fibers with mechanical properties close to the ones of virgin fibers. Solvolysis is a process able to treat all types of composites, no matter their geometry, density, surface quality, size, etc. Princaud studied the solvolysis with sub- and supercritical water, with a temperature between (300-450)°C and 25 MPa. The water is principally used to prevent cooking and enhance the decomposition of the resin.[62]

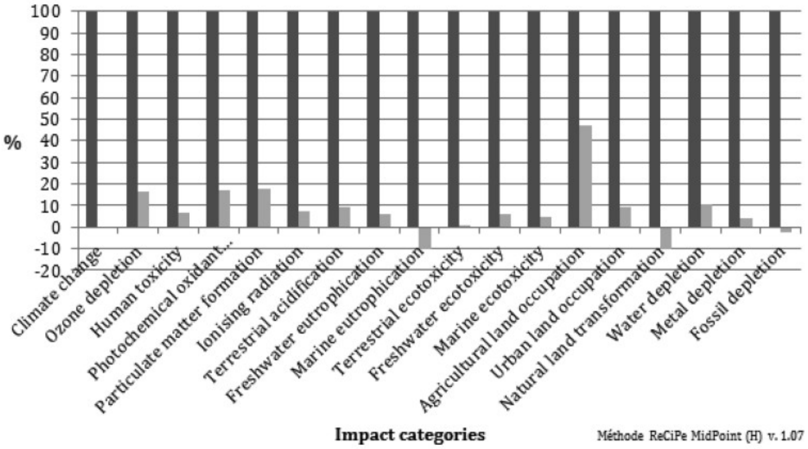


Figure 3.11: Comparison of the environmental impacts (landfill in dark gray, recycling in light gray). Image extracted from: Environmental feasibility of the recycling of carbon fibers from CFRPs by solvolysis using supercritical water.[62]

In figure 3.11 can be appreciated the environmental impact of 1 kg of composite CF, depending on the end-of-life scenario (landfill or recycling CF). Pricaud also showed that the second generation carbon fibers (recycled) don't exceed in the price of (70 M-80) percent of the new ones.[62]

Faced with the need for efficient and low-cost carbon fiber, alternative precursors to PAN are constantly sought, and more than 50% of the cost is attributed to the precursor. With the lack of efficiency of other precursors, researchers are looking for other ways to improve the physical properties of carbon fibers. It's known the spinning and stabilization process controls the orientation, alignment, and crystallization of the microstructure and chain polymer. To optimize these processes, can be added compounds into the polymer matrix. The addition of 1.0 wt % CNTs can improve the strength in 64 % and lowered the carbonization temperature (as reported Chae. 2007). The addition of graphene (2D) shows better properties than CNTs, such as tensile strength, Young modulus, superior electron mobility, and larger surface area. These advances can not only be applied to PAN carbon fibers but to any kind of fiber, in this way fibers with precursors could be produced cheaper than PAN and with excellent properties.[63]

The addition of graphene to the matrix of PAN carbon fibers changes the microstructure and increases the Young modulus, strain, strength, also can reduce the pore size and voids. The unique parameter that remained unaffected is the fracture strain. A determining factor is the amount of graphene concentration, the best concentration is 0.075 wt %. It concentration present a Young's modulus of 233 GPa and tensile strength of 1915 MPa. If the concentration of graphene is increased to 0.1 wt % present a reduction in the fiber properties to 980 Mpa of tensile strength. It means that passing a critical content the composite properties being to deteriorate. Analyzing these changes in the carbon fibers in a structural way, it was observed that they without graphene exhibit elongated axial micropores. If the graphene is added, the prevalence of these micropores is reduced without introducing nanoporosity.[63]

In the Figure 3.12 can be appreciated how the micropores are reducing according to the concentration of graphene.

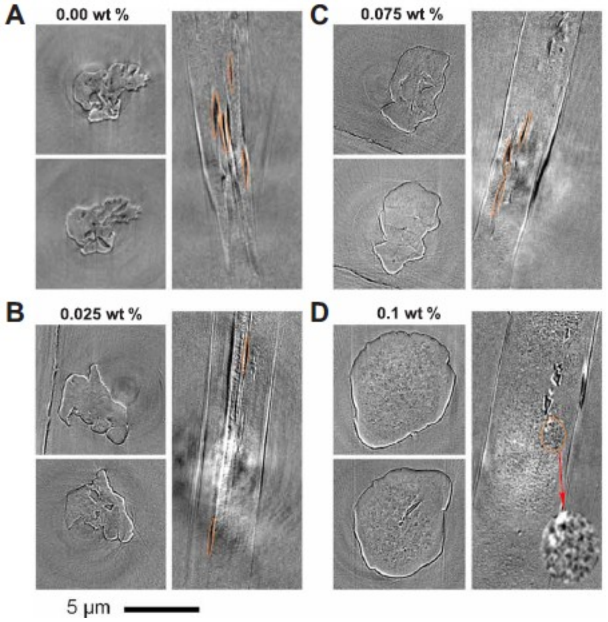


Figure 3.12: Nanotomography measurement of PAN/graphene composite CFs. Levels of graphene content. Image extracted from "graphene reinforce carbon fibers"[63]

Examining the viscosity was found that it gradually increases with the graphene concentration from 0.01 to 0.075 wt %. When the concentration of graphene reached 0.1 wt % a decrease in viscosity was found. It is due to the increase in viscosity help to align the graphene nanosheets in the spinning process, this can guide the solidification during the coagulation process leading to minimize the voids and pores.[63]

3.1 Applications

Carbon fibers have been developed and improved throughout history from its initial application as filaments in electric lamps to the present day, where it is used in a wide variety of industries such as automotive, sporting, aerospace, military, among others. There are two ways in the carbon fiber applications, the first way is the use of virgin carbon fiber such as adsorbents, electrodes, biomedical applications, and catalysts. The second way is used, they are fiber-reinforced composites.[48]

The virgin carbon fibers are mostly used in activated forms through physical or chemical activation processes. Their activation provides meso- and micropores that lead to the high surface area, good electrical, and physicochemical properties. The Active carbon fibers (ACF) in general are used as adsorbents for organic molecules (bacteria, viruses, organic vapors), filters (face mask, protective clothing, combat gear), liquid purification, air conditioning, enzyme and catalyst support, bandages, blood purification among other applications.[1]

The pores present in carbon fibers can be used as hydrogen storage where pore geometry and pore size distribution control gas compression and sorption/desorption reaction rate. Other applications of pores are water and air purification, and solvent recovery. This process is carried out through adsorption processes.[64]

Another amazing application is the carbon fibers can be used as energy storage as full cells, supercapacitor, and lithium battery. In the fuell cells the carbon fiber can be used like electrode materials, electrical reinforcements, substrates and so on. It is possible because the energy storage devices transform the chemical energy into electricity through a reaction. The continuous advancement in technology has required the development of more efficient and economical supercapacitors. The advantage that provides the carbon fiber is working as an electrode material because its surface area that provides good microstructures and electrochemical properties. The application of carbon fibers in lithium batteries like alternate anode for lithium metal provides several advantages as long cycle life, low electrode potential, safety. The pitch-based carbon fibers are used for this kind of application due it "Skin-core" that consists of two crystalline structure regions.[65]

The carbon fibers are so popular in manufacturing industries because their mechanical properties give them good flexibility and lightweight.[49] One example of this is the aircraft industry, where the composites are fabricated using sandwich construction. Generally, the fibers used in the interior part of planes have high fire-resistant properties, low flammability, low smoke emission, and low gas toxicity. There are big differences between the aircraft and automobiles carbon fibers. For the aircraft industry, the high performance is the most important and the cost is negligible. While, for automobile industry the high performance is the main factor to consider and cost is the principal variable.[1] These kinds of factors affect the performance and price of the fibers to be produced.

Nowadays, the wind turbine blades are made of carbon fibers providing rigid, lightweight, good fatigue resistance, and long duration (10-year service life). In sport, carbon fibers are used in golf clubs, windsurfing masts, hockey sticks, bicycle stands, rackets, rods, snowboards, backpacks, tent poles, baseball bats, and so on. Carbon fibers are used in all kinds of sectors, in construction the carbon fibers achieve improved flexural strength, tensile strength, compressive strength, drying, and toughness. The most common composite is the mixture with cement-matrix.[56]

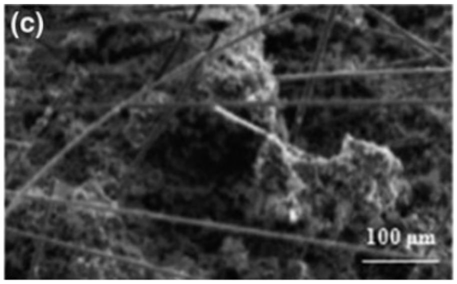


Figure 3.13: SEM micrographs of carbon fibers distributed in cement matrix. Image extracted from "High strength and high modulus carbon fibers"[56]

Chapter 4

Conclusions

The discovery of the great applications of carbon fibers has been a great milestone in the history of mankind. From its beginnings as filaments in electric lamps until today, where most of the industrial sectors make use of these, they have been developing and managing to provide unique properties to their composites. It is possible to affirm that the most important precursor is PAN, other precursors like rayon have no commercial importance.

When we talk about characterization techniques, if we need a non-destructive technique, we can use Raman: which through its modes indicates the G-, D-, D'-, 2D-lines bands which it gives us the structural fingerprint, by which can be identified the molecules that compose and also represent hexagonal ring structures, symmetry or disorders structures, degree of graphitization. The Raman spectroscopy is ideal to make strain measurements in carbon fibers.[28] The (STM) is used to take two-dimensional images of carbon fibers at the nanometric level. It can bring us 0.1 nm of lateral resolution and 0.01 nm of depth resolution. The analysis of carbon fibers with its technique can show the surface structure (if it is: bulk) or if it has microstructures. It allows us to observe the atomic resolution of the fibers, where the carbon atoms generally stand out as bright points.[31] The atomic force microscopy (AFM) is especially useful when a detailed surface of carbon fiber is needed. It is very similar to STM but is preferable to use the AFM since it requires less preparation in the sample, in addition it can be used both in conductors and insulators, therefore the carbon fibers do not need any coating.[33] UV-vis spectroscopy is not commonly used to characterize the fibers themselves, but it is used to characterize certain precursors or dopants that will be used in their manufacture. The Scanning Electron Microscopy

(SEM) is used to take high-resolution images of surface carbon fibers. It can bring us 0.4 - 20 nm of resolution. The analysis of carbon fibers with its technique can show the surface texture (if it is: smooth or rough) or morphological structure. The problem with this technique is that the sample needs to be conductive.[31] These are the characteristics and advantages that the characterization techniques offer us. Bearing this in mind can help us for the correct analysis of the fibers and optimization of resources.

A small change in some step or characteristic of a precursor causes a big change in the final properties of the fibers. In this way, the industries consider all small details in their manufacture, these variables can be molecular weight, crystallinity, distribution, orientation, and impurities. This leads companies to prefer to manufacture their own precursors and use their own manufacturing procedures (adding additives, resins coatings, and post spinning treatments).[49]

A fiber is spun with approximately 3000 to 50'000 of filaments. The spun fiber can be defined like precursor fiber from the carbon fibers. There is the possibility to convert nonheterocyclic aromatic polymers into carbon fibers with advantages, such as high-temperature resistance, good carbon yield, easy clearing of contaminants, and easy cyclization into the graphitic structure, but the principal drawback is their high cost. The possible strength of carbon fibers (high quality) is 100 GPa, but actually the commercial carbon fibers have a maximum of 7 GPa. But normal (common) carbon fibers have only 10-60% of their tensile strength.

The yield of rayon carbon fibers is very low compared to PAN, it can be between 10-30 %. The more efficient precursor is PAN among cellulose, pitch, rayon, and so on. One way to increase the carbon yield is the use of flame retardants because the decomposition of cellulose occurs at lower temperatures and faster rate, leading to better carbon yield. Precursors can play the most important role in the preparation, due to the fact that the modulus and strength of carbon fibers are directly related to the precursor stretch-ratio. However, the properties of carbon fibers deteriorate in a very high draw-ratio. The stabilization process corresponding to spinning can determine the orientation, crystallization, and alignment of the chain polymer used and the microstructure of precursors, which affect the mechanical properties of the final carbon fibers. Also, it is important to consider that surface properties of carbon fibers are intimately related to the graphitic basal plane.

The graphitization temperature manufacture of CF shows that a lower temperature has a high ratio of micropores and a less organized surface structure (increasing the surface area). Higher temperatures result in a reduction of micropores and a decrease in the surface area. The interlinked turbostratic nature of crystals serves as a crack hindrance mechanism. That is why the local fault failure of crystals that occurs before the catastrophic failure of the fiber, resulting in higher tensile strength.[66]

Talking of composites, the adhesion between matrix and fibers is one of the most important factors. The adhesion is determined by surface fiber properties and matrix properties. Carbon fibers occupy the largest volume fraction in fiber-reinforced composites. The fibers bear most of the load of the composite, this load is transferred from the matrix to the fibers through the interface.[66]

The mechanical properties of carbon fibers are what make them so attractive in different industrial sectors. It is known that they do not suffer from stress rupture failure or stress corrosion at room temperature. Also, in carbon fiber composites for the industry of mobility they provide fuel savings due to the low density of the parts, which means that there is less weight to move, which means less fuel consumed and therefore money savings. They are ideal for applications in which stiffness, strength, outstanding fatigue, and low weight are critical requirements. Another important characteristic is that they have good high-temperature resistance, good chemical inertness, good tensile strength, and young modulus.

Appendix A

Glossary

1. **Spinning polymers:** It is a form of extrusion that uses a spinneret to form filaments.[67]
2. **Extrusion:** It is a process where a material is pushed or pulled through a die of the desired cross-section.[68]
3. **Pascal (Pa):** is a unit of pressure of the International System of Units that corresponds to $1Pa = 1\frac{kg}{m*s^2}$.[69]
4. **Newton (N):** is a unit of force in the International System of Units that corresponds to $1N = 1\frac{kg*m}{s^2}$.[69]
5. **Pyrolysis:** is the thermal decomposition of materials (change in chemical composition) at high temperatures and inert atmospheres.[70]
6. **Isotropy:** is the characteristic of materials where the properties do not depend on the direction in which they are examined. Similar results are obtained regardless of the direction chosen.[71]
7. **Anisotropy:** is the characteristic of materials where the properties do depend on the direction in which they are examined. different results are obtained regardless of the direction chosen.[71]
8. **Turbostatic:** is a characteristic of carbon layers where they are arranged in a messy or random manner.[72]

9. **Clusters:** Clusters consist of a small number of atoms, at most in the tens. These nanoclusters can be composed of one or more elements, and are typically less than 2 nm in size, and exhibit attractive electronic, optical and chemical properties compared to their larger counterparts.[73]

10. **Amphiphilic molecule:** is a molecule that have a hydrophilic end (soluble in water), and another hydrophobic end (repels water).[74]

Bibliography

[1] Park, S.-J. Carbon fibers. **2015**,

[2] Das, S.; Warren, J.; West, D.; Schexnayder, S. M. *Global carbon fiber composites supply chain competitiveness analysis*; 2016.

[3] Senplades, Plan nacional de desarrollo 2017 – 2021 "Toda una vida". *Ecuador Desarrollo* **2017**,

[4] Bhushan, B. *Springer handbook of nanotechnology*; Springer, 2017.

[5] del Castillo Rodriguez, F. D. Introduccion a los Nanomateriales. *Facultad de Estudios Superiores Cuautitlán (UNAM) Departamento de Ingeniería Laboratorio de Tecnología de Materiales* **2012**, 1–76.

[6] Bowen, W. R.; Hilal, N. *Atomic force microscopy in process engineering: An introduction to AFM for improved processes and products*; Butterworth-Heinemann, 2009.

[7] Hirsch, A. *Fullerenes and Related Structures*; Springer, 1999; pp 1–65.

[8] Hulla, J.; Sahu, S.; Hayes, A. Nanotechnology: History and future. *Human & experimental toxicology* **2015**, *34*, 1318–1321.

[9] Donnet, J.-B.; Bansal, R. C. *Carbon fibers*; Crc Press, 1998.

[10] Thangadurai, T. D.; Manjubaashini, N.; Thomas, S.; Maria, H. J. *Nanostructured Materials*; Springer, 2020.

[11] García-Betancourt, M. L.; Jiménez, S. I. R.; González-Hodges, A.; Salazar, Z. E. N.; Escalante-García, I. L.; Aparicio, J. R. Low Dimensional Nanostructures: Measurement and Remediation Technologies Applied to Trace Heavy Metals in Water. **2020**,

[12] Saito, T. *Inorganic Chemistry*; CreateSpace Independent Publishing Platform, 2014.

[13] Pauling, L. The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules. *Journal of the American Chemical Society* **1931**, *53*, 1367–1400.

[14] Peschel, G. Carbon-carbon bonds: hybridization. *Obtained online from: http://www. physik. fu-berlin. de/einrichtungen/ag/ag-reich/lehre/Archiv/ss2011/docs/Gina_Peschel-Handout. pdf, published on* **2011**, *5*.

[15] Klyachko, A. A. The Pauli exclusion principle and beyond. *arXiv preprint arXiv:0904.2009* **2009**,

[16] Narang, P.; Garcia, C. A.; Felser, C. The topology of electronic band structures. *Nature Materials* **2021**, *20*, 293–300.

[17] Oliveira, F. Photonic integrated circuit (PIC) devices for inter-and intra-chip optical communication using GeSn alloy layers grown on Silicon substrates.

[18] Kittel, C. Introduction to solid state physics Eighth edition. **2021**,

[19] Smallman, R. E.; Bishop, R. J. *Modern physical metallurgy and materials engineering*; Butterworth-Heinemann, 1999.

[20] Jastrzebski, Z. D. Nature and properties of engineering materials. **1976**,

[21] Lim, H.; Hoag, S. W. Plasticizer effects on physical–mechanical properties of solvent cast Soluplus® films. *Aaps Pharmscitech* **2013**, *14*, 903–910.

[22] Zhang, X.; Sun, C.; Fang, N. Manufacturing at nanoscale: Top-down, bottom-up and system engineering. *Journal of Nanoparticle Research* **2004**, *6*, 125–130.

[23] Aliofkhazraei, M.; Ali, N.; Milne, W. I.; Ozkan, C. S.; Mitura, S.; Gervasoni, J. L. *Graphene science handbook: Fabrication methods*; CRC Press, 2016.

[24] Jasti, R.; Bertozzi, C. R. Progress and challenges for the bottom-up synthesis of carbon nanotubes with discrete chirality. *Chemical physics letters* **2010**, *494*, 1–7.

[25] Rawat, R. Dense plasma focus-from alternative fusion source to versatile high energy density plasma source for plasma nanotechnology. 2015.

[26] Bhushan, B.; Luo, D.; Schricker, S. R.; Sigmund, W.; Zauscher, S. *Handbook of nanomaterials properties*; Springer Science & Business Media, 2014.

[27] Chee Ho, K. K.; Qian, H.; Bismarck, A. Carbon fiber: surface properties. *Wiley encyclopedia of composites* **2011**, 1–11.

[28] Washer, G.; Blum, F. Raman spectroscopy for the nondestructive testing of carbon fiber. *Research Letters in Materials Science* **2008**, *2008*.

[29] Smith, E.; Dent, G. *Modern Raman spectroscopy: a practical approach*; John Wiley & Sons, 2019.

[30] Wiesendanger, R.; Güntherodt, H.-J. *Scanning tunneling microscopy III: theory of STM and related scanning probe methods*; Springer Science & Business Media, 2013; Vol. 29.

[31] Wu, Q.-L.; Gu, S.-Y.; Gong, J.-H.; Pan, D. SEM/STM studies on the surface structure of a novel carbon fiber from lyocell. *Synthetic metals* **2006**, *156*, 792–795.

[32] Rugar, D.; Hansma, P. Atomic force microscopy. *Physics today* **1990**, *43*, 23–30.

[33] Dilsiz, N.; Wightman, J. Surface analysis of unsized and sized carbon fibers. *Carbon* **1999**, *37*, 1105–1114.

[34] Stan, C. V.; Beavers, C. M.; Kunz, M.; Tamura, N. X-ray diffraction under extreme conditions at the Advanced Light Source. *Quantum Beam Science* **2018**, *2*, 4.

[35] Warren, B. E. *X-ray Diffraction*; Courier Corporation, 1990.

[36] König, U.; Angélica, R. S.; Norberg, N.; Gobbo, L. Rapid X-ray diffraction (XRD) for grade control of bauxites. *ICSOBA Proceedings* **2012**, *19*, 11pp.

[37] Wazir, A. H.; Kakakhel, L. Preparation and characterization of pitch-based carbon fibers. *New carbon materials* **2009**, *24*, 83–88.

[38] BV, D. C.; HYDRAULICS, D. Absorption spectroscopy. **1962**,

[39] Slavík, J. Absorption Spectroscopy. *Intracellular pH and its Measurement* **1989**, 69.

[40] Nakayama, Y.; Soeda, F.; Ishitani, A. XPS study of the carbon fiber matrix interface. *Carbon* **1990**, *28*, 21–26.

[41] Stevie, F. A.; Donley, C. L. Introduction to x-ray photoelectron spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2020**, *38*, 063204.

[42] Lee, W.; Lee, J.; Reucroft, P. XPS study of carbon fiber surfaces treated by thermal oxidation in a gas mixture of O2/(O2+ N2). *Applied Surface Science* **2001**, *171*, 136–142.

[43] Zhou, W.; Wang, Z. L. *Scanning microscopy for nanotechnology: techniques and applications*; Springer science & business media, 2007.

[44] Yao, S.; Hai, L.; Shuiquan, P.; Zhu, B.; Zhang, X.; Fatikow, S. A Review of Computer Microvision-Based Precision Motion Measurement: Principles, Characteristics, and Applications. *IEEE Transactions on Instrumentation and Measurement* **2021**, *PP*, 1–1.

[45] Popov, V. N. Carbon nanotubes: properties and application. *Materials Science and Engineering: R: Reports* **2004**, *43*, 61–102.

[46] Harik, V. *Mechanics of Carbon Nanotubes: Fundamentals, Modeling and Safety*; Academic Press, 2018.

[47] Young, R. J.; Lovell, P. A. *Introduction to polymers*; CRC press, 2011.

[48] Huang, X. Fabrication and properties of carbon fibers. *Materials* **2009**, *2*, 2369–2403.

[49] Bajpai, P. In *Carbon Fiber (Second Edition)*, second edition ed.; Bajpai, P., Ed.; Elsevier, 2021; pp 13–50.

[50] Dumanlı, A. G.; Windle, A. H. Carbon fibres from cellulosic precursors: a review. *Journal of Materials Science* **2012**, *47*, 4236–4250.

[51] Dotson, N. A.; Galvan, R.; Laurence, R. L.; Tirrell, M. *Polymerization process modeling*; John Wiley & Sons, 1995.

[52] Frank, E.; Hermanutz, F.; Buchmeiser, M. R. Carbon fibers: precursors, manufacturing, and properties. *Macromolecular materials and engineering* **2012**, *297*, 493–501.

[53] Matsumoto, T. Mesophase pitch and its carbon fibers. *Pure and applied chemistry* **1985**, *57*, 1553–1562.

[54] Kubo, S.; Kadla, J. Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties. *Journal of Polymers and the Environment* **2005**, *13*, 97–105.

[55] Xu, Z.; Gao, C. Graphene fiber: a new trend in carbon fibers. *Materials Today* **2015**, *18*, 480–492.

[56] Chae, H. G.; Newcomb, B. A.; Gulgunje, P. V.; Liu, Y.; Gupta, K. K.; Kamath, M. G.; Lyons, K. M.; Ghoshal, S.; Pramanik, C.; Giannuzzi, L. High strength and high modulus carbon fibers. *Carbon* **2015**, *93*, 81–87.

[57] Thostenson, E.; Li, W.; Wang, D.; Ren, Z.; Chou, T. Carbon nanotube/carbon fiber hybrid multiscale composites. *Journal of Applied physics* **2002**, *91*, 6034–6037.

[58] Chand, S. Review carbon fibers for composites. *Journal of materials science* **2000**, *35*, 1303–1313.

[59] Xuetao, S.; Kezhi, L.; Hejun, L.; Hongying, D.; Weifeng, C.; Fengtao, L. Microstructure and ablation properties of zirconium carbide doped carbon/carbon composites. *Carbon* **2010**, *48*, 344–351.

[60] Kumar, S.; Doshi, H.; Srinivasarao, M.; Park, J. O.; Schiraldi, D. A. Fibers from polypropylene/nano carbon fiber composites. *Polymer* **2002**, *43*, 1701–1703.

[61] Wang, G. X.; Han, H.; Li, L. W.; Quan, H. Y.; Shi, Y. P.; Qin, W. Z.; Lu, P.; Wu, Q. L. SEM and AFM studies on the surface and cross section morphology of rayon-based activated carbon fibers. 2011.

[62] Princaud, M.; Aymonier, C.; Loppinet-Serani, A.; Perry, N.; Sonnemann, G. Environmental feasibility of the recycling of carbon fibers from CFRPs by solvolysis using supercritical water. *ACS Sustainable Chemistry & Engineering* **2014**, *2*, 1498–1502.

[63] Gao, Z.; Zhu, J.; Rajabpour, S.; Joshi, K.; Kowalik, M.; Croom, B.; Schwab, Y.; Zhang, L.; Bumgardner, C.; Brown, K. R. Graphene reinforced carbon fibers. *Science advances* **2020**, *6*, eaaz4191.

[64] Ermolenko, I. N.; Lyubliner, I.; Gulko, N. V. Chemically modified carbon fibers and their applications. **1990**,

[65] Fukai, J.; Kanou, M.; Kodama, Y.; Miyatake, O. Thermal conductivity enhancement of energy storage media using carbon fibers. *Energy Conversion and Management* **2000**, *41*, 1543–1556.

[66] Chung, D. D. *Applied materials science: applications of engineering materials in structural, electronics, thermal, and other industries*; CRC Press, 2001.

[67] Zhang, D. *Advances in filament yarn spinning of textiles and polymers*; Elsevier, 2014.

[68] Wick, C.; Benedict, J.; Veilleux, R. Tool and Manufacturing Engineers Handbook: Forming, Vol. 2. *Society of Manufacturing Engineers, Dearborn, MI* 4–1.

[69] Kittel, C.; McEuen, P.; McEuen, P. *Introduction to solid state physics*; Wiley New York, 1996; Vol. 8.

[70] Alemán, J.; Chadwick, A. V.; He, J.; Hess, M.; Horie, K.; Jones, R. G.; Kratochvíl, P.; Meisel, I.; Mita, I.; Moad, j. v. n. p. y. p., G Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials (IUPAC Recommendations 2007).

[71] Kocks, U. F.; Tomé, C. N.; Wenk, H.-R. *Texture and anisotropy: preferred orientations in polycrystals and their effect on materials properties*; Cambridge university press, 1998.

[72] Shallcross, S.; Sharma, S.; Kandelaki, E.; Pankratov, O. Electronic structure of turbostratic graphene. *Physical Review B* **2010**, *81*, 165105.

[73] Chen, W.; Chen, S. *Functional nanometer-sized clusters of transition metals: Synthesis, properties and applications*; Royal Society of Chemistry, 2014; Vol. 7.

[74] Streitwieser, A.; Heathcock, C. H.; Kosower, E. M.; Corfield, P. J. *Introduction to organic chemistry*; Macmillan New York, 1992.

Abbreviations

ACF Activated carbon fibers 59
AFM atomic force microscopy 25

CFs Carbon Fibers 51
CLTE Coefficient of linear thermal expansion 35
CNTs Carbon Nanotubes 51, 61

GFs Graphene Fibers 51

HG High modulus 47
HT High strength 47

IM Intermediate modulus 47

LM Low modulus strength 47

MP Mesophase pitch 35, 36

PAN Polyacrylonitrile 35, 36, 52

RACF rayon-based activated carbon fiber 59
RCF rayon carbon fibers 59

SEM scanning electron microscopy 31
STM Scanning tunneling microscope 24

UHM Ultra-high modulus 47

XPS X-ray Photoelectron Spectroscopy 30
XRD X-ray Disfraction 26