Surface Treatment of Softwood Lignin Based Carbon Fibers for Enhanced Interfacial Adhesion

Effects of Plasma Treatment Parameters on the Creation of Surface Groups

Yunus Can Gorur

Materials Science Engineering, Masters Level
2017

Luleå University of Technology
Department of Engineering Sciences and Mathematics
Student:

Yunus Can Gorur
AMASE Master Program in Materials Science Engineering,
Luleå University of Technology, Sweden
Ecole Europeenne d’Ingenieurs en Genie des Materiaux, EEIGM
Université de Lorraine, France

Examiner:

Professor Roberts Joffe
Polymeric Composite Materials
Division of Materials Science
Luleå University of Technology, Sweden

Supervisors:

Birgitha Nyström – Tommy Öman
Swerea SICOMP
Piteå, Sweden

This project has received funding from the Bio Based Industries Joint Undertaking under the European Union’s Horizon 2020 research and innovation programme under grant agreement No 667501.
Acknowledgements

I would like to express my sincere gratitude to my examiner Professor Roberts Joffe and my supervisors Birgitha Nyström and Tommy Öman for the continuous support of my MSc thesis studies and related research, for their patience, motivation, and immense knowledge. I could not have imagined having better people to work with and supervise my MSc studies. Besides my examiner and supervisors, I would also like to thank Daniel Eklund at Swerea SICOMP for all the help and expertise he has provided during this project. Last but not least, I would like to thank my family for supporting me physically and spiritually throughout my thesis studies.

Yunus Can Gorur
Luleå, December 2016
Abstract

Lightweight design is an essential part of lowering CO$_2$ emission, which is one of the most important challenges that the automotive industry is facing today. Carbon fiber reinforced plastics offer an enormous potential for replacing heavier structural materials like steel and aluminum, however due to their high cost and scarcity, carbon fibers are not a very feasible option to use in high volume production applications. It is thought that the introduction of a renewable, low-cost raw material, like lignin, as the carbon fiber precursor would not only lower the cost but also increase supply compared to its PAN based counterparts. Properties of the fiber/matrix interface play a crucial role in governing the overall performance of the composite material. Good adhesion between the fiber and the matrix must be ensured in order to maximize performance. In this study, plasma treatment of softwood lignin based carbon fibers was performed in order to increase the interfacial adhesion between the fiber and the matrix by incorporating functional groups onto the fiber surface. Plasma treatment time, plasma power, chamber pressure and plasma gas type were varied in order to investigate their effects on the functionalization of the surface by various visual, chemical and mechanical characterization methods. Observations with optical and scanning electron microscopies showed the cleaning effects of plasma treatment on the fiber surface by removal of flakes and smoothing of the fiber surface. The smoothing effect of plasma treatment was later supported by the subtle increase in the tensile strength of the plasma treated fibers and this was attributed to the elimination of crack initiators on the surface by a so-called “polishing” effect. Contact angle measurements of the lignin based fibers showed that all plasma gases achieve a certain level of decrease in the contact angle values thus lowering the surface tension. X-ray photoelectron spectroscopy (XPS) results were analyzed using a design of experiments software with a PLS fit. For the highest amount of surface functionality to be achieved, it was concluded that oxygen plasma should be used with high plasma power, low pressure and a high treatment time. Detection of Na and S elements combined with unusually low mechanical properties for all lignin based carbon fibers indicated insufficient carbonization or molecular orientation for the softwood lignin based carbon fibers used in this study.
# Contents

1. **Introduction** .......................................................................................................................... 4  
   1.1. The GreenLight Project ................................................................................................. 4  
   1.2. The Scope of the Master's Thesis ................................................................................... 5  
2. **Background** ............................................................................................................................ 6  
   2.1. Carbon Fiber Surface Treatment Methods ..................................................................... 9  
      2.1.1 Wet Chemical Methods ............................................................................................. 10  
      2.1.1.1 Polymer Sizing ..................................................................................................... 10  
      2.1.1.2 Liquid Phase Oxidation ....................................................................................... 11  
      2.1.1.3 Electrochemical Modification .............................................................................. 14  
      2.1.2 Dry Modifications ...................................................................................................... 16  
      2.1.2.1 Plasma Treatment .................................................................................................. 16  
      2.1.2.2 High Energy Irradiation Modification .................................................................. 20  
      2.1.3 Multi-scale Methods ..................................................................................................... 21  
      2.1.3.1 Nano Particles Modification .................................................................................. 21  
      2.1.3.2 Carbon Nano-tube Coating .................................................................................. 22  
   2.2 Conclusions .......................................................................................................................... 24  
   2.3. Interfacial Adhesion in CFRP ............................................................................................ 26  
   2.4. Experimentation Technique ........................................................................................... 29  
   2.5. Carbon Fiber Characterization Techniques ..................................................................... 30  
      2.5.1 Scanning Electron Microscopy (SEM) ..................................................................... 31  
      2.5.2 X-ray Photoelectron Spectroscopy (XPS) ................................................................ 31  
      2.5.3 Contact Angle Measurements ................................................................................. 31  
      2.5.4 Single Fiber Tensile Tests ......................................................................................... 31  
      2.5.5 Single Fiber Fragmentation Tests (SFFT) ................................................................. 31
3. Experimental..................................................................................................................................................35
  3.1 Materials ..................................................................................................................................................35
  3.2 Surface Treatment Methods Employed ......................................................................................................35
  3.3 Sample Preparation for Tensile Tests ........................................................................................................37
  3.4 Sample Preparation for Single Fiber Fragmentation Tests .........................................................................37

4. Results and Discussion....................................................................................................................................40
  4.1 Optical Microscopy (OM) ..........................................................................................................................40
  4.2 Scanning Electron Microscopy (SEM) .......................................................................................................41
  4.3 X-ray Photoelectron Spectroscopy (XPS) ..................................................................................................44
  4.4 Contact Angle Measurements ..................................................................................................................57
  4.5 Single Fiber Tensile Tests .......................................................................................................................58
  4.6 Single Fiber Fragmentation Tests ............................................................................................................63

5. Conclusions ....................................................................................................................................................64

6. Appendix ........................................................................................................................................................65
  6.1 Machine Compliance Analysis ..................................................................................................................65
  6.2 Weibull Analysis .......................................................................................................................................66

7. References ......................................................................................................................................................68
1. Introduction

1.1. The GreenLight Project

Lowering the CO\textsubscript{2} emission is one of the most important challenges that the automotive industry is facing today. Since reducing the vehicle weight plays a significant role in lowering fuel consumption and increasing distance per energy input, the most straightforward approach to achieve lower CO\textsubscript{2} emission is to lower the vehicle weight. Carbon fiber reinforced plastics (CFRP) is a high-performance low-weight material that can replace or complement heavier structural materials like steel and aluminum without compromising safety in the automotive industry. On the other hand, CFRP comes at a higher cost compared to its traditional counterparts due to high precursor costs of petroleum based Polyacrylonitrile (PAN). Moreover, expected market volumes by 2020 indicate that the future supply capacity of PAN will struggle to meet the demand. It is thought that the introduction of a renewable, low-cost raw material would solve both of these problems at the same time. Several companies such as Volkswagen, along with universities and institutes around the world have identified lignin as a possible replacement option for the expensive and non-renewable petroleum based PAN. The largest industrial source of lignin is the kraft pulp and paper industry, which handles about 40 million tons of kraft lignin (12 million of which in Europe) worldwide. Thanks to a new technology invented by Innventia and Chalmers University of Technology in Sweden and commercialized by Valmet (the LignoBoost process), lignin is an industrially abundant biopolymer that is now separated as by-product commercially at kraft pulp mills.

Nine organizations from four different countries are participating in the GreenLight project in order to undertake the challenge of developing cost effective lignin-based carbon fibers for innovative light-weight applications. The GreenLight project will tailor kraft lignin for lignin-based carbon fiber and develop a way to introduce this new lignin-based carbon fiber in the existing value chain, hence connecting the pulp and paper industry to the automotive sector while enabling a novel high technology industry to expand in Europe. The overall goal of GreenLight is to demonstrate a new bio-based and economically viable carbon fiber precursor (lignin) and to develop conditions for its processing into carbon fibers and eventually to carbon fiber composites. The target is a cost-efficient sustainable carbon fiber reinforced composite with suitable strength properties; specifically for high volume automotive applications.
1.2. Scope of the Master’s Thesis

The subject thesis work is focused on the research and application of appropriate surface treatment methods for lignin-based carbon fibers in order to improve fiber/matrix adhesion in the resulting composite material. Surface treated carbon fibers are to be characterized visually (SEM, OM) and chemically (XPS) in order to observe the evolution of surface roughness and creation of functional groups on the fiber surface. Characterized carbon fibers are then to be tested for their mechanical properties (SFTT) to study the quality of the fiber/matrix interface (Contact Angle). Various surface treatment methods will be tested throughout the thesis project with an emphasis on plasma surface treatment technologies.
2. Background

Lightweight design makes up an essential part of the general design strategies for increasing performance and reducing CO₂ emissions in a variety of industries today. Especially in the transportation sector, namely aviation and automotive, lightweight structures play a significant part in lowering operational and environmental costs while increasing the performance without actually having to change the existing engine technologies. The aforementioned physical advantages of lightweight design combined with the emission standards set by political and environmental pressures make lightweight design an important asset in achieving a variety of design targets. This is mainly because of the fact that the emission standards set for the near future will not be achieved by improvements in engine technologies alone (Fig. 1). The use of carbon fiber reinforced polymers (CFRP) provides a tremendous lightweight potential compared to the traditional materials like aluminum (Al) and steel. For the case of the automotive industry, using a load adapted CFRP design could provide weight reduction up to 60% without actually compromising functionalities and safety [1].

![Figure 1: CO₂ emission standards in Germany [1]](image)

Carbon fiber reinforced polymer (CFRP) composites started to be used for commercial production in the 1960s. They offered a good lightweight structural alternative for a wide range of potential applications, especially in aviation and automotive industries, thanks to their superior properties such as high specific strength and stiffness, performance to weight ratio, high thermal stability, high conductivity, self-lubrication, and corrosion resistance [2]. CF reinforced polymers in the beginning were used predominantly in high performance applications such as military and aerospace. As the CFRP production became more popular, automotive industry (luxury and sports cars) started replacing some of the traditional structural materials with lightweight CF reinforced polymers. However, the penetration of CFRP into the automotive industry has started to stall recently due to the maximization of gains in the current phase for production. Although the use of CFRP oriented design provides many advantages in the name of performance and environment; it is still a fairly expensive solution and therefore cannot be commercialized to an extent where it will provide high
volume gains in the industry yet. Specifically in the automotive industry lightweight construction provides a reduction of fuel consumption, an increase in range, as well as better driving dynamics in conjunction with the two previous advantages (Fig. 2). On the other hand, these weight benefits cannot be utilized fully in mass series applications due to the high cost of carbon fiber production. Another important issue with the current conventional carbon fiber production is that the demand in the market is forecasted to exceed the supply by 2020 [3]. This problem calls for a solution to decrease carbon fiber production costs, especially to meet the demand in high volume applications that do not require aerospace grade carbon fiber e.g. automotive, wind turbine blades. Currently polyacrylonitrile (PAN) is the most commonly used precursor in the production of carbon fibers. When the overall production cost of carbon fibers is examined, it is noted that more than 50% of the production costs are related to the raw material and its transformation into precursor fibers (Fig. 3) [1,4]. Evidently, finding a cheaper and more abundant alternative raw material for the production of the precursor would not only reduce the production costs but also could support the carbon fiber supply that is under pressure by the increasing market demand.

![Figure 2: Weight reduction spiral in automotive industry [1]](image)

![Figure 3: Cost distribution for the production of PAN-based carbon fiber [1]](image)
Lignin is an aromatic biopolymer and it has gathered substantial attention in the past as a possible alternative precursor candidate due to its high carbon content, low cost, and sustainable nature. The molecular structure of lignin consists of repeating units of phenylpropane, which makes it highly polar with a large number of hydroxyl (-OH) groups. However, the production of lignin based carbon fiber has been stalled because of the difficulties in processing of lignin fibers [4]. Thielemans and Wool [5] focused on the effects of esterification on the solubility of lignin for polyester resins. Later on, Kessler et al. [4] also modified lignin by esterification in order to improve its molecular level miscibility with PLA to prepare lignin/polylactide blends to produce bio-renewable carbon fiber precursors. Lignin as a raw material to make carbon fiber precursors has many advantages over conventional raw materials. Lignin is bio-based, renewable, and potentially available in large quantities since it is present in virtually all fibrous plants. Kraft pulping is the most popular method in the paper industry to make paper and most paper products require lignin to be removed during the early stages of the process, which means that lignin basically becomes a waste product following its removal. Therefore, using lignin to produce carbon fiber precursors would not only provide large quantities of raw material but also it would provide this material at a very low cost. Combined with the sustainable and bio-friendly nature of lignin compared to its petroleum based counterparts, lignin highlights itself as a very good alternative raw material to be used in the making of carbon fiber precursors.

According to the difference of structures, lignin can be categorized into three different classes, which are hardwood lignin, softwood lignin, and grass lignin. Hardwood lignin is composed of syringyl (S) and guaiacyl (G) units and softwood lignin consists predominantly of G units, while grass lignin is a mix of S, G, and p-hydroxyphenyl (H) units (Fig. 4) [6]. Origin of the lignin macromolecule plays a significant role in terms of processability of the resulting precursor. In contrast to hardwood lignin, softwood lignin is not easily melt spinnable into fibers and chars upon heating due to its insufficient thermoplastic characteristics, which prevents it from reaching its real mechanical capabilities [7]. Aside from the difficulties in processing, just like any carbon fiber product, lignin based carbon fibers require a certain amount of surface treatment in order to improve their interfacial properties in a composite. On the other hand, so far there are no reports specifically addressing the conditions for surface treatment of lignin-based carbon fiber, especially softwood lignin. This section aims to review the research work conducted over the past couple of years in the field of carbon fiber surface modifications and carbon fiber/polymer interfacial adhesion in order to provide an up-to-date account of various carbon fiber surface treatment methods.
2.1. Carbon Fiber Surface Treatment Methods

Although carbon fiber is an excellent reinforcement for polymers, aside from being quite expensive, it is well known that CFRCs also exhibit somewhat poor interfacial adhesion between fibers and epoxy matrix due to a chemically inert carbon fiber surface and low surface energy of the carbon fibers [8]. Hence, there are almost no chemical bonds or physical interactions such as van der Waals, hydrogen bonding or mechanical interlocking, which leads to poor interfacial shear properties [9]. Motivated by this problem, many researchers tackled this issue of poor interfacial adhesion by surface treating carbon fibers in different ways. Therefore extensive studies were conducted with different surface treatment methods including gas phase, liquid phase and anodic oxidation; polymer coating (sizing) and plasma treatment methods in order to improve the interfacial adhesion [2,10].

Surface treatment of carbon fibers can work in two ways, which usually take place simultaneously, to enhance the adhesion between the matrix and the carbon fiber. Physically, surface treatment can introduce or enhance surface roughness by increasing the surface area in order to provide more contact points for a better mechanical interlocking. Chemically, surface modification can promote active functional groups on the carbon fiber surface to ensure good chemical bonding between the fiber and the polymer matrix [2]. However, it is very important to establish an optimum level of surface treatment. It should always be kept in mind that any kind of surface treatment, especially the type that etches the fiber surface, will have adverse effects on the mechanical properties of the fiber. Furthermore, an interfacial bond that is too strong will cause the composite to be excessively brittle, which is not a desirable situation, for most cases where composites are needed in fact demand a certain level of ductility [10]. Different surface treatment methods can promote an improved fiber/matrix adhesion via different mechanisms. Most common mechanisms involve boosting the wettability of the fiber surface [11], removing the weak outermost layer on the fiber to eliminate surface
contaminants in order to ensure better contact for van der Waals interactions [10], allowing matrix molecules to entangle with or diffuse into the molecular network of the polymer sizing applied on the fiber [12], promoting mechanical interlocking between the fiber and the matrix via increasing surface porosity to ensure resin penetration onto the fiber surface [13], and increasing the amount of active sites via incorporation of functional groups onto the fiber surface [14].

Carbon fiber surface treatment methods can be studied under three major categories, which are wet chemical methods, dry modifications, and multi-scale modifications [2].

2.1.1. Wet Chemical Methods

2.1.1.1. Polymer Sizing

Sizing refers to a resin or thin polymeric coating applied onto the surface of the carbon fiber to improve the fiber processability, which also alters the way that the load is transferred from a failed fiber to an intact one via modified fiber/matrix interface (Fig. 5) [12,15]. The critical surface flaws formed during textile processing can act as a stress concentrator for crack propagation and must be minimized, on the other hand application of sizing can protect the brittle fibers, improve fiber/sizing/matrix adhesion, and provide strand integrity [2]. Hence, the main goal in sizing application is to insert a polymer interlayer between the carbon fiber and the matrix that would govern the level of fiber/matrix adhesion by changing the surface energetics to increase wettability for better fiber/matrix adhesion [16]. Sizing application can be achieved via various methods such as deposition from solution of a polymer, electrodeposition, deposition via electropolymerization, and plasma polymerization [10]. Factors like fiber/sizing compatibility [17], sizing molecular weight [18], and presence of coupling agents [12] play a significant role in determining the interfacial shear strength properties of the resulting composites.

Figure 5: Diagram of a sizing line. (1 - unwinding mechanism; 2 - tension adjustment unit; 3 – bath; 4 – sprayer; 5 - drying box; 6 - drawing mechanism; 7 – winding mechanism; 8 – motor and speed control; 9 – reservoir circulation) [51]
Numerous studies have been conducted on the effects of sizing application on carbon fiber and its adhesion performance with respect to the subject matrix material. Wightman et al. [16] studied and compared the surface properties of sized and unsized carbon fibers. AFM results indicated that the application of sizing on the carbon fiber surface altered the surface roughness values. However, sizing application also lowered the surface energy and decreased both the polar and dispersive components along with the percentage of functional groups on the fiber surface (Fig. 6). It should be kept in mind that surface functional groups and surface energies of fibers are deciding factors in fiber/matrix adhesion. Weitzsacker et al. [15] demonstrated that the chemistry of the sizing changes after application to the treated fibers. Naturally, such chemical changes on the surface also alter the adhesion performance of the fiber. The study concluded that any examination on the surface and interface chemistry of carbon fibers or carbon fiber reinforced composites should be conducted on unsized carbon fibers. Aside from the chemical structure, molecular weight of the sizing is an important factor in fiber/sizing compatibility. Zhang et al. [18] examined the effect of sizing molecular weight on the fiber/matrix interface properties by sizing carbon fibers with three different molecular weight epoxy sizing agents and then analyzing the surface topographies, surface energies, and interfacial shear strength (IFSS) values of the resulting carbon fibers and their composites. Although further confirmation is needed, the researchers concluded that lower molecular weight sizings are more compatible compared to their high molecular weight counterparts that form interfaces that are too rigid and hence exhibit brittle behavior.

![Figure 6: The percentage of functional groups on unsized and sized carbon fibers [16]](image)

2.1.1.2. Liquid Phase Oxidation

Strong acid treatment is a commonly used wet method to introduce functional groups onto the carbon fiber surface to increase surface hydrophilicity (Fig. 7). Increasing the surface polarity or active sites for van der Waals interactions and Hydrogen bonding can improve the interfacial adhesion between the fiber and the matrix, which in turn would ensure a better stress transfer from the matrix to the fiber [19]. Aside from increasing surface polarity, acid treatment also corrodes the carbon fiber surface while introducing perforations for better mechanical interlocking between the fiber and the matrix [20]. On the other hand, acid
concentration and treatment time must be optimized carefully in order avoid the adverse effects of the treatment. Prolonged acid treatment, while introducing functional groups to the surface, simultaneously induces pits, crevices, and flaws on the surface, which reduces single fiber strength to a significant extent [10].

*Figure 7: Surface functionalization via acid treatment [24]*

There is a variety of liquid phase oxidizing agents that have been used to surface treat carbon fibers such as HNO$_3$ [20,23], NaOH [20], NaOCl [10], KMnO$_4$ [21], NaClO$_3$ [10], maleic anhydride (MA) [22], and NaIO$_4$ [10] in the past. Amongst various liquid oxidizing agents for fiber surface treatment, nitric acid (HNO$_3$) treatment is the most classical method to introduce surface functional groups on the surface and etch it to improve fiber/matrix interactions as a result of the increase in surface area and surface energy [23]. One of the main goals in surface treating carbon fibers with HNO$_3$ is to create oxygenated surface functional groups such as –COOH, –OH, –C=O on the carbon fiber surface [19]. There are numerous studies on the effects of nitric acid treatment on the interfacial behavior of carbon fibers. Ryu et al. [20] surface treated activated carbon fibers with 1 M nitric acid and observed that the pore volume and the surface area decreased. It was thought that the decrease in surface area was due to decreased micropore volume resulting from pore blocking done by surface oxide groups forming in some of the micropores. Although the observations seemed to be counterintuitive, the researchers concluded that this was due to the sensitivity of the activated carbon towards nitric acid. On the other hand, oxidation treatment led to a significant increase in terms of surface oxide groups such as carboxyl, lactone, and phenol. Aside from oxygenated functional groups, it is known that amino groups react rapidly with epoxides [24]. Knowing this, attempts were made at trying to introduce a high surface amine concentration onto carbon fibers in order to enhance adhesion between carbon fiber and epoxy matrix. Pittman et al. [24] surface treated polyacrylonitrile (PAN) based carbon fibers with nitric acid oxidation followed by reaction with excess tetraethylenepentamine (TEPA) to generate acidic functions such as carboxyl and phenolic hydroxyl groups, which were then reacted with TEPA at 190° - 200° C to introduce surface bound amino-functions. The idea was to replace the carboxyl groups on the surface with more reactive amino functions by reacting them together to increase total amount of surface bound functional groups (Fig. 8). An average of 2.59 amino groups were introduced for each acidic group consumed and the average ratio of the total amino groups introduced to the total amount of acidic groups present after nitric acid oxidation was approximately 1.35, which basically indicated a 35% increase as a result of TEPA treatment.
Severini et al. [22] studied surface properties of unsized carbon fiber treated with aqueous ammonia. Basic groups were introduced onto the surface as a result of reactions with Diels Alder reagents such as maleic anhydride. XPS analysis indicated strong nitrogen content even though untreated samples had zero nitrogen content. It was observed that the basic groups introduced to the fiber enhanced the adhesion between the fiber and the epoxide matrix as measured by the single fiber method, suggesting an improvement in the fiber/matrix stress transfer performance. Xu et al. [21] modified carbon fibers by acrylic acid treatment with the help of physical energy from γ-ray irradiation in order to develop a convenient and inexpensive method to increase the interfacial wettability and adhesion without sacrificing mechanical properties of carbon fibers. The surface of the modified fiber was observed to be rougher and there was an increase of oxygen content on the fiber surface. These observations were followed by an increase in the fiber surface energy and in the number of the carbonyl, carboxyl and/or ester functional groups. Hence, wettability of the treated carbon fibers were improved along with significant improvements in interlaminar shear strength (ILSS) values (Fig. 9).

**Figure 8: Introduction of amino groups via reaction with carboxyl group [24]**

**Figure 9: Effect of surface modification on ILSS and tensile strength of CF/epoxy composites [21]**
2.1.1.3. **Electrochemical Modification**

Electrochemical surface modification utilizes the electron transfer phenomenon to alter the oxidation state and functionalize the surface of the carbon fiber while increasing its surface energy and roughness, hence significantly improving its adhesion to the matrix polymer. Compared to other surface treatment methods, electrochemical modification is preferred for being relatively simple to control and allowing the continuous processing of carbon fibers, which makes anodization one of the most practical surface treatment methods for commercial production of carbon fibers (Fig. 10) [14,25]. It is for this reason that when carbon fibers were introduced in a continuous form, anodic oxidation became the favored method of surface treatment, for it utilizes the conductive aspect of carbon fiber to act as an anode in a suitable electrolyte bath to functionalize the fiber surface [10].

![Diagram of electrochemical treatment apparatus](image)

**Figure 10: Diagram of electrochemical treatment apparatus [25]**

Fukunaga et al. [14] electrochemically oxidized pitch-based carbon fibers in 0.1 M NH₄HCO₃ in order to investigate the mechanism of anodic surface oxidation. It was found that the values measured by coulostatic method could be used for monitoring the effect of the anodic surface oxidation because there was a good correlation between the change in the differential double-layer capacity \( (C_d) \) determined by the coulostatic method and ILSS. The mechanism of anodic oxidation for pitch-based carbon fibers was proposed to be selective oxidation and the appearance of prismatic surfaces in crevices, which have many sites that are chemically active towards epoxy resin, ensuring better fiber/matrix adhesion (Fig. 11). Yue et al. [27] electrochemically oxidized PAN-based carbon fibers serving as an anode by applying current in 1% wt aqueous KNO₃ and examined the treated carbon fibers using XPS, FTIR, aqueous NaOH titration, and weight loss measurements upon heat treating to characterize the effects of electrochemical oxidation on the fiber surface chemical composition and morphology. Fiber weight loss was observed to increase with progressive electrochemical oxidation and NaOH uptake demonstrated that acidic functions were generated in direct proportion to the extent of oxidation up to a certain plateau value. XPS results showed a rise primarily in carboxyl (COOH) or lactone (COOR) groups upon oxidation. The untreated carbon fiber samples exhibited no significant weight loss after heat treatment, unlike the treated samples, following the electrochemical treatment. This weight loss was due to thermal decomposition of oxygenated functions that have been formed in direct proportion to the extent of
electrochemical oxidation, which also means that the weight loss values could be used to quantify the extent of surface functionalization to a certain extent.

![Figure 11: Proposed model for the mechanism of surface oxidation of pitch-based carbon fiber [14]](image)

Although it is well-known that in composites both mechanical and chemical effects should be taken into account when studying the interfacial bonding between the matrix and the fiber, the chemical effect of oxygen-containing functional groups (–COOH, –OH, –C=O) on the surface is thought to be stronger than the mechanical effect of rough surfaces [14]. Therefore, the functional groups to be created on the carbon fiber surface must be chosen carefully. The type and amount of the functional groups formed depend on the type and concentration of the electrolyte used along with the treatment time and applied voltage [26]. Sodium hydroxide, sodium chloride, ammonium hydrogen carbonate, ammonium carbonate, sulfuric acid, and nitric acid are commonly used electrolytes to introduce oxygen functionalities on the carbon fiber surface. [2,10] Similar to liquid phase oxidation method, treatment time also plays an important role in electrochemical modification. Despite its advantages, electrochemical modification technique also has a confirmed disadvantage that the treatment process will reduce the tensile strength of carbon fibers while increasing the interfacial adhesion between the fiber and the matrix [25]. Hence, precise control and optimization of the electrochemical process parameters is essential. Recent work has been conducted on the electrochemical modification process in order to further improve it and minimize its disadvantages. One of the anomalies that puzzled the scientists was the observation that even though electrochemical oxidation decreased the crystallite size, which should have had a positive effect on the tensile strength due to grain refining effect, it actually reduced the tensile strength. Liu et al. [25] performed electrochemical oxidation on PAN based carbon fibers in (NH₄HCO₃)/(NH₄)₂C₂O₂·H₂O aqueous compound solution to improve the tensile strength and interfacial bonding strength simultaneously. The results indicated that the tensile strength of the fibers could be increased by 17.1% while ILSS showed a 14.5% improvement. Furthermore, after electrochemical oxidation it was observed that the crystallite size
decreased by 23-27\% and ordered degree on carbon fiber surface increased with suitable etching, which actually did not peel off the ordered region to create new cracks, hence increasing the tensile strength. It was concluded that suitable etching can increase tensile strength; while excessive etching peels of the ordered region and exposes the inner disordered region, creating new cracks and hence leading to lower tensile strength. Porosity of the carbon fiber surface also attracted the attention of the scientific community. Pores in carbon fibers are thought to be extremely narrow spaces between crumpled sheets of intertwined carbon layers which expose little surface area and pore volume, which makes probing the porosity a difficult task. Leon et al. [28] investigated the surface area and pore size distribution of electrochemically oxidized PAN-based fibers and concluded that many carbon fibers contain pores that are too small to allow their adequate characterization by standard nitrogen adsorption at 77K or by mercury porosimetry and suggested that such small pores (ultramicropores) could be effectively probed by CO$_2$ adsorption at 273 K.

2.1.2. **Dry Modifications**

2.1.2.1. **Plasma Treatment**

Plasma is defined as an electrically conducting medium generally consisting of negatively charged electrons, positively charged ions, and neutral atoms or molecules or both [29]. Plasma is produced by inserting dielectric insulation between metal electrodes and applying high frequencies and voltage to accelerate the electrons emitted from the electrodes in an electric field by corona discharge (Fig. 12) [30]. Hence, it can be said that plasma is a quasi-neutral gas of charged and neutral particles containing cations and electrons. According to the gas temperature of various plasmas, they are generally divided into two groups, which are high-temperature plasma and low-temperature plasma. Cold plasma (gas temperature below 1000 K) is a sub group of low-temperature plasmas and it is a promising surface treatment tool. The success of cold plasma in surface treatment of carbon fibers relies on its very high electronic temperature and relatively low gas temperature; as the former leads to a chemical modification on the surface and the latter, being as low as room temperature in most cases, allows fibers to experience such surface modification without the reduction in mechanical properties [29]. As mentioned before, the chemical effect of oxygen-containing functional groups (–COOH, –OH, –C=O) on the surface is thought to be stronger than the mechanical effect of rough surfaces [14]. Plasma treatment, particularly low-temperature oxygen plasma, provides a means of conveniently introducing surface oxygen functional groups rapidly and cleanly on carbon surfaces with minimal burn-off and structural damage to the bulk and the near surface. In most cases plasma only modifies the outermost layers of the fiber because the low activation energy needed by atomic oxygen species to react with carbon atoms does not allow these oxygen species to diffuse towards the internal surface [31]. Furthermore, the treatment time needed to achieve the desired changes in fiber chemistry is of the order of
several seconds to a few minutes, thus plasma treatment has the advantage that many samples, or very long samples, can be treated reliably with the help of a continuous conveyor belt, lowering the processing time and cost to a great extent [30,31].

Figure 12: Corona discharge cell. (1 – high voltage source; 2,3 – electrodes; 4 – sample; 5 – ground connection) [51]

Typical gases used to create plasma include gases like O₂ [31-35,40], N₂ [36], Ar [37], acetylene [38], air [39], isobutylene [40]. Due to the aforementioned advantages of plasma surface treatment, it has been studied extensively in the past. Tascón et al. [31] performed oxygen plasma treatment on pitch-based isotropic carbon fibers and characterized the plasma treated fibers via scanning electron microscopy (SEM), scanning tunneling microscopy (STM), N₂/CO₂ adsorption, Raman spectrometry, and X-ray photoelectron spectroscopy (XPS) to investigate the effects. SEM observations showed that even for the most intense treatments, the external surface remained smooth and the fibers kept their initial diameter (Fig. 13). Only the flakes that were observed pre-treatment, which were associated with contamination during processing, tended to disappear after the plasma treatment indicating the “cleaning” effect of plasma treatment. STM revealed topographical transformations upon plasma-induced etching, which involved a general increase in nanometer scale surface roughness. A comparison of the results for surface areas and pore volumes calculated from N₂ and CO₂ adsorption tests indicated that the plasma treatment led to the formation of very narrow pores, which show up on CO₂ adsorption but do not show up on N₂ adsorption due to the larger size of the N₂ molecules. A comparison of the surface atomic O/C ratios and bulk atomic O/C ratios via XPS before and after plasma treatment revealed that although before the treatment the two ratios were similar to each other, after the treatment the surface O/C ratio increased significantly whereas the bulk O/C ratio remained basically the same (Fig. 14). This was attributed to diffusion limitations in the plasma oxidation process causing the treatment effects to stay on the surface and not affect the fiber as a whole.
Pittmann et al. [40] surface treated PAN-based carbon fibers with oxygen and isobutylene plasmas to study the effects of exposure time, plasma power and gas pressure on the quantity of acidic functional groups introduced onto the fiber surfaces post-treatment and their relation to carbon fiber surface areas, interfacial shear strengths (IFSS) and interlaminar shear strengths (ILSS). It was observed that an optimum pressure (0.2 Torr at 50 W and 1.2 Torr at 400 W at the conditions employed) exists for oxygen plasma treatment of carbon fibers under which the largest amount of surface acidic functions can be generated. Moreover, acidic functions were observed to form rapidly and reach a maximum in approximately 2 to 5 minutes of oxygen plasma treatment (20 to 200 W) while longer exposure reduced the quantity of surface acidic functions. It was reported that oxygen plasma treatment led to improvements in interfacial adhesion and hence the interlaminar shear strength while it did not reduce the fiber tensile strength. Schwartz et al. [38] evaluated the effects of acetylene/oxygen plasma treatment of carbon fibers on the torsional fatigue of composite strands made from the treated fibers and concluded that even though the improvement was not as pronounced as it was in the interfacial shear strength, it was still statistically significant.
Fukunaga et al. [37] performed oxygen and argon plasma treatments on pitch-based carbon fibers in order to compare the results to those of anodized fibers. It was reported that the plasma treated samples obtained a much higher adhesive strength to an epoxy resin than did the anodized samples. Crystalline size of the surface was observed to become smaller (change from 13.2 nm to 4.4 nm) and according to coulstatic method, $C_d$ and $R_p$ values indicated that apparent surface area and active surface area of the plasma treated samples increased to a significant extent compared to the anodized samples. Plasma treated samples had higher ILSS values compared to the anodized samples and it was noted that all specimens of the failure mode for oxygen plasma treated samples were the bending mode (the crack is perpendicular to the fiber axis), not the shear mode (the crack is parallel to the fiber axis) indicating a much stronger adhesion for oxygen plasma treated samples than the measured value as ILSS. In relation to these findings, the proposed mechanism of plasma treatment was unlike that of anodization, the surface layer was peeled and the aromatic bonds in the basal plain were cleaved by plasma etching leading to a considerable increase in terms of active sites on the surface, thus enabling strong adhesion to epoxy resin (Fig. 15). Lee et al. [30] studied the effects of plasma surface treatment of recycled carbon fiber on adhesion of the fiber to polymers after various treatment times. Surface functionalization was quantified using an XPS and the team achieved an O/C increase of approximately 11% to 25% with just 0.5 seconds of treatment time or less, supporting the view that plasma treatment is a very promising method in terms of industrial efficiency for scale-up operations. Springer et al. [32] focused on the changes in thermodynamic surface properties such as wettability, solid surface tension, and the electrokinetic $\zeta$-potential of PAN-based carbon fibers following an oxygen plasma surface treatment. They reported that a short treatment time (1 min) led to a large decrease in measured contact angle values and an increase in surface acidity. Hence it was concluded that the surface polarity and therefore the hydrophilic character of the carbon fibers as well as the adsorption potentials of ions were increased upon oxygen plasma treatment.

Figure 15: Schematic models of anodization and plasma treatment mechanisms [37]
2.1.2.2. High Energy Irradiation Modification

In high-energy irradiation treatment, the fibers are exposed to high energy, usually gamma, irradiation or laser irradiation, which leads to surface roughening along with the addition of functional groups such as carbonyl onto the fiber surface. It is thought that radiation affects the crystal lattice by displacement of atoms within the lattice or by electronic excitation and the electrons stripped from the atoms are believed to cause topographical change of carbon fibers while creating active sites on fiber surfaces, which may react with functional groups of bulk matrix polymers [41]. The technology of high-energy irradiation is widely used in the field of material interface modification due to its high efficiency, energy conservation, and environmentally friendly nature [42]. Although plasma surface treatment is a prevalent method today, it also has its own drawbacks such as need for high facilities, high energy consumption, and high maintenance costs compared to high-energy irradiation [43]. High-energy irradiation has many unique advantages over conventional surface treatment methods that make it desirable for carbon fiber surface treatment applications. High-energy irradiation can induce chemical reactions at any temperature in all phases without the help of a catalyst, it is a safe method that does not contribute to environmental pollution, it can be used to treat carbon fibers that are out of the production line, it can reduce curing time and save energy, and it could treat three dimensional samples regardless of its shape thanks to its superior penetration capabilities [44]. Currently there are two main radiation types that are being used in the industry, which are gamma and e-beam. Huang et al. [44] treated PAN-based carbon fibers with Co\textsuperscript{60} \(\gamma\)-ray irradiation and reported a 37% improvement in the interlaminar shear strength (ILSS) values of the treated carbon fiber/epoxy composites. XPS analysis revealed a rapid increase in the O/C ratio with the start of the treatment and AFM results indicated that the degree of roughness was increased under relatively lower absorbed doses (30 kGy) whereas excess irradiation (>250 kGy) had negative effects on the mechanical interlocking between the carbon fiber and the epoxy resin. These findings were later supported by Li et al. [42] who studied the surface performance PAN-based carbon fibers irradiated by \(\gamma\)-ray under different irradiation doses. They reported that the graft rate increased with increasing absorption dose but excessive absorption dose and graft rate were not beneficial to the interface performance (Fig. 16). Xu et al. [43] graft polymerized three kinds of monomers onto carbon fiber surface with the aid of physical energy from \(\gamma\)-ray irradiation in order to enhance the carbon fiber/epoxy interface. The team reported significant improvements in terms of surface roughness and number of oxygen containing functional groups, especially carbonyl, carboxyl and ester, along with the surface energy. Although the tensile strength was observed to improve marginally, interlaminar shear strength (ILSS) was enhanced by at least 17.5% compared to that of untreated carbon fiber/epoxy composite.
2.1.3. Multi-scale Methods

2.1.3.1. Nano Particles Modification

Chemical bonding theory suggests that rare earth elements are adsorbed onto both the carbon fiber surface and the matrix through chemical bonding, which increases the concentration of reactive functional groups due to the chemical activity of these rare earth elements, leading to improved fiber/matrix compatibility and enhanced interfacial adhesion [45]. Similar to other surface treatment methods, the main goal in nano particles modification is to enhance interfacial adhesion by means of increasing the surface roughness and introducing surface functional groups. Huang et al. [46] soaked and irradiated PAN-based carbon fibers in praseodymium nitrate—Pr(NO$_3$)$_3$—solution to compare their effects on the surface physiochemical properties of carbon fibers. The team reported that both immersion and irradiation led to an increase in fiber surface roughness, an increase of oxygen-containing surface functional groups, the enhancement of the degree of disorder, and the introduction of praseodymium element on the carbon fiber surface. These findings were further supported by the increasing interlaminar shear strength (ILSS) values. Finally, it was concluded that irradiation treatment was superior to the immersion treatment in terms of promoting interfacial properties due to its capability to increase carboxyl and carbonyl groups on the surface to a greater extent (Fig. 17).
Xu et al. [47] investigated the effects of different rare earth (praseodymium nitrate) concentrations on the interfacial properties of carbon fiber/epoxy composites. It was found that rare earth treatment led to an increase in surface roughness along with the carbonyl in ketones, quinines and carboxyl or ester functional groups, while causing a decrease in graphitic carbon and phenolic or ether oxygen functional groups. In relation to these observations, 0.5% rare earth-treated carbon fibers showed a 15.8% improvement in ILSS, which was attributed to the increase of carboxyl and carbonyl groups on the fiber surface. A similar study by Cheng et al. [45] investigated the effects of rare earth concentration to understand the rare earth treatment mechanism. The rare earth solution (RES) concentration was varied from 0.1 wt% to 0.5 wt% and it was seen that the tensile strength and modulus increased with increasing RES concentration, reaching the maximum value at 0.3 wt% and then decreasing gradually with the further increase of RES concentration. This behavior was explained by monomolecular layer theory, stating that when free lanthanides exist in the interface due to excess concentration, adhesion force between the two surfaces is reduced due to the existence of weak van der Waals forces leading to decreasing tensile properties for the composite (Fig. 18).

![Figure 18: The model of monomolecular layer theory. (a) 0.1wt% RES (b) 0.2wt% RES (c) 0.3wt% RES [45]](image)

2.1.3.2. Carbon Nano-tube Coating

Growing carbon nanotubes (CNT) on the surface of high performance carbon fibers provides means to tailor the thermal, electrical, and mechanical properties of the fiber-resin interface of a composite with the possible side effect of degrading tensile properties due to harsh growth conditions [48]. CNTs can be incorporated onto the fiber surface parallel or vertical to the load direction. CNTs are 100-times stronger than steel but their density is six times lower than that of steel’s and these features combined with the CNTs superior thermal properties make them an attractive reinforcement option for carbon fiber composites [49]. The real use of CNTs in composites for structural applications, however, has been disappointing despite a promising start, due to issues such as poor dispersion, alignment and interfacial strength [50]. CNTs have been grown by various methods such as electric arc-discharge, laser ablation, and chemical vapor deposition (CVD) [48]. Kepple et al. [49] investigated the interlaminar
properties of a three dimensional (3D) composite system made using CNTs grown perpendicular to the fiber axis to improve bonding between the fiber and the matrix. Substantial improvements (50%) in terms of fracture toughness were achieved in the cured composite along with no loss in structural stiffness of the final composite structure. In fact, the flexural modulus was observed to increase by 5% along with a significant increase in fracture toughness. Mathur et al. [50] grew CNTs via chemical vapor deposition (CVD) on different carbon fiber substrates such as unidirectional (UD) carbon fiber tows, bi-directional (2D) carbon fiber cloth and three dimensional (3D) carbon fiber felt. Enhanced mechanical properties were observed on all hybrid substrates with addition of only 5 wt% CNT. Baur et al. [48] grew high density multi-wall carbon nanotubes (MWCNT) on sized and unsized PAN-based carbon fibers via thermal chemical vapor deposition (CVD) to investigate the influence of CVD growth conditions on the single-fiber tensile properties and CNT morphology. The mechanical properties of the resultant hybrid fibers were observed to depend on the carbon fiber used, the presence of sizing on the fiber, the CNT growth temperature and time, and atmospheric conditions inside the CVD chamber. Overall, unsized fibers responded to the treatment better in terms of retaining their tensile properties while enhancing their interfacial properties compared to their sized counterparts.
2.2. Conclusions

Based on the literature review conducted, surface treatment of carbon fibers is essential for ensuring good adhesion behavior with various matrix materials. Different types of surface treatment methods and their effects on various parameters are summarized in Table 1 and Figure 19. The following observations were made for all surface treatment methods during the review;

- Surface treatment alters the fiber surface morphology and increases surface roughness
- Increased surface roughness almost always leads to increased surface area, which provides more contact points for mechanical interlocking between the fiber and the matrix
- Surface treatment introduces functionalized surface groups on the fiber surface that enhance chemical bonding between the fiber and the matrix
- Optimization is required for all surface treatment methods since excessive treatment may have degrading effects on the fiber mechanical properties
- Although different treatments have different effects on the fiber surface, the main idea behind surface treatment consists of the above-mentioned effects
<table>
<thead>
<tr>
<th>Treatment Type</th>
<th>Surface Area/Roughness</th>
<th>Surface Groups</th>
<th>Surface Energy</th>
<th>ILSS</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Sizing</td>
<td>Subtle increase in surface roughness</td>
<td>Decrease in the amount of functional groups</td>
<td>Decrease in surface energy</td>
<td>Relative increase in ILSS</td>
<td>Increase in tensile strength due to elimination of critical surface flaws</td>
</tr>
<tr>
<td>Liquid Phase Oxidation</td>
<td>Substantial increase in surface roughness and surface area. Introduction of deep perforations and ridges</td>
<td>Introduction of oxygenated functional groups such as COOH, –OH, –C=O</td>
<td>Increase in surface energy</td>
<td>Improvements in ILSS</td>
<td>Prolonged treatment has adverse effects on the mechanical properties</td>
</tr>
<tr>
<td>Electrochemical Modification</td>
<td>Increase in surface area by generation of micropores</td>
<td>Introduction of functional groups, mainly carboxyl and lactone</td>
<td>Increase in surface energy</td>
<td>Improvements in ILSS</td>
<td>Prolonged treatment has adverse effects on the mechanical properties</td>
</tr>
<tr>
<td>Plasma Treatment</td>
<td>Introduction of perforations and subtle increase in roughness. Surface modification rather than bulk effects</td>
<td>Introduction of hydroxyl, ether and carbonyl functional groups</td>
<td>Increase in surface energy</td>
<td>Improvements in ILSS</td>
<td>Minimal burn-off and structural damage to the fiber even with prolonged treatment</td>
</tr>
<tr>
<td>High Energy Irradiation</td>
<td>Increased surface roughness by displacement of atoms. Excess irradiation makes the surface smoother, which prevents mechanical interlocking</td>
<td>Introduction of carbonyl, carboxyl, and ester functional groups</td>
<td>Increase in surface energy</td>
<td>Improvements in ILSS</td>
<td>Marginal increase in tensile strength for low irradiation doses</td>
</tr>
<tr>
<td>Nano Particles Modification</td>
<td>Increased surface roughness by means of added nanoparticles</td>
<td>Introduction of sulfonic, carbonyl, hydroxyl, and carboxyl functional groups</td>
<td>Increase in surface energy</td>
<td>Improvements in ILSS</td>
<td>Subtle improvements in tensile strength</td>
</tr>
<tr>
<td>CNT Coating</td>
<td>Increase in surface roughness and surface area via growth of CNTs perpendicular to the fiber axis</td>
<td>No reported change in the amount of surface groups</td>
<td>No reported change in the surface energy</td>
<td>Improvements in ILSS</td>
<td>Tensile properties may degrade due to harsh CNT growing conditions</td>
</tr>
</tbody>
</table>

Table 1: Summary of the surface treatment methods and their effects
2.3. Interfacial Adhesion in CFRP

Composites technology is based on taking advantage of the stiffness and strength of high-performance fibers by dispersing them in a matrix, which acts as a binder and transfers forces to the fibers across the fiber/matrix interface [52]. Therefore, the properties of fiber/matrix interface play a crucial role in governing the overall performance of the composite material since a successful reinforcement in composite materials is only achieved by ensuring sufficient stress transfer between the fiber and the matrix. In order to replace the phenomenological understanding of adhesion, tribology and interfacial/fracture mechanics by specific atomic or molecular scale mechanisms, scientific efforts have been focused on the analysis of interfacial phenomena and the resulting properties for many years. Several researchers have investigated the influence of interfacial strength and the quality of adhesion on overall performance of composites [53,54]. Eventually the interphase concept was introduced into the literature. As a result of physical and chemical interactions between the fiber and the matrix, a nano-meter length scale thin layer forms between them during processing of composites, which is referred to as an interphase (Fig. 20) [55]. The properties of composites are critically based on the microstructure and performance of this interphase. Fiber and matrix phases might be combined chemically or mechanically at the interphase, which can be seen as a diffusion zone, a chemical reaction zone or a nucleation zone, a thin layer of fiber sizing or coating, or any combination of the above [56]. A better interfacial bond between the fiber and the matrix will impart better properties to the composites such as the interlaminar shear strength (ILSS), delamination resistance, and fatigue and corrosion resistance.
The basic structure of a typical carbon fiber consists of long primary units (lateral aromatic molecules) lying parallel to the fiber axis and bonding together to form a stretched network of branched fibrils that apparently run the full length of the fiber. Some carbon fibers exhibit a skin/core structure, meaning that the surface structure is different than the core structure. This could be a result of higher preferred orientation in the skin area leading to a relatively high density of material near the fiber surface, or a gradient of oxidation between the outer and inner portions may have formed during the stabilization steps [56]. Most of the carbon fiber surface is composed of graphite basal planes, whose size is dictated by the manufacturing temperature and exposure time. During the manufacturing of the carbon fibers higher temperature and longer exposure times lead to larger graphite planes and larger layered crystallites on the fiber surface, while the tension imposed on the fiber might cause the fibrils to align better with respect to the fiber axis, hence making the surface made entirely of graphitic basal planes with low reactivity. This high preferred orientation on the surface makes the carbon fibers, especially the high modulus ones, very inert to chemical reaction and modification.

Most surface treatment methods essentially aim to introduce disorder to the surface structure to make the surface more reactive by increasing the surface free energy. One of the most straightforward ways of achieving this is to functionalize the surface via some type of oxidation method (chemical, electrochemical, plasma). Increased surface free energy with the incorporation of surface functional groups in turn makes the carbon fiber surface more reactive towards the resin, ensuring better interfacial bonding (Fig. 21). Aside from the surface energy, oxidation also etches the surface and increases the surface area of the carbon fiber by introducing surface roughness. On the other hand, the surface roughness on a few tens of nanometer scale has no significant contribution to interphase adhesion from a “mechanical interlocking” perspective. In contrast, the true contact area on the nanometer scale plays a dominant role in interfacial adhesion [57].

Figure 20: Interface and interphase of fiber reinforced composite [56]
The total surface energy, $\gamma_i$, can be split into two components, the Lifshitz-van der Waals ($\gamma_i^{LW}$) and the acid-base component ($\gamma_i^{AB}$). The former represents the dispersion forces, dipole interactions (Keesom) and induction (Debye), and the latter represents the H-bonding or acid-base interactions. This is written as the sum of the two components;

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}$$  \hspace{1cm} (1)

and for the liquid

$$\gamma_L = \gamma_L^{LW} + \gamma_L^{AB}$$  \hspace{1cm} (2)

where the acid-base term is

$$\gamma_L^{AB} = 2(\gamma_L^{+}\gamma_L^{-})^{1/2}$$  \hspace{1cm} (3)

The subscript (S) denotes the solid phase and the subscripts (plus and minus signs) denote the surface free energy contributions due to the Lewis acid and Lewis base components respectively. Similarly, the acid base component of the liquid phase is denoted with the subscript L,

$$\gamma_L^{AB} = 2(\gamma_L^{+}\gamma_L^{-})^{1/2}$$  \hspace{1cm} (4)

Then the adhesion between the solid and liquid is given as;

$$(1 + \cos \theta) \gamma_L = 2(\gamma_L^{LW}\gamma_S^{LW})^{1/2} + \gamma_{SL}^{AB}$$  \hspace{1cm} (5)

$$\gamma_{SL}^{AB} = 2[(\gamma_S^{+}\gamma_L^{-})^{1/2} + (\gamma_S^{-}\gamma_L^{+})^{1/2}]$$  \hspace{1cm} (6)
The Lifshitz-van der Waals component \((\gamma_{SL}^{LW})\) of the surface energy is

\[ \gamma_{SL}^{LW} = [(1 + \cos \theta) \gamma_L]^2 / 4 \gamma_L^{LW} \]  

(7)

The acid-base interaction term can then be found by rearranging eqn (5)

\[ \gamma_{SL}^{AB} = (1 + \cos \theta) \gamma_L - 2(\gamma_L^{LW} \gamma_{SL}^{LW})^{1/2} \]  

(8)

The acid-base component is related to the polar functional groups attached to the edges and corners of graphitic basal planes. Therefore, incorporation of polar groups onto the carbon fiber surface has direct effect on the surface free energy of the fiber. High modulus fibers tend to have lower surface free energy due to the increased carbonization temperature that enlarges the inert graphitic basal plane area, which in turn diminishes the presence of surface chemical groups. Reintroduction of these functional groups via surface treatment restores the required polarity to ensure adequate fiber/matrix adhesion in the composite.

2.4. Experimentation Technique

Designed experiments were chosen over the traditional one-factor-at-a-time (OFAT) experiments, which vary only one factor at a time while keeping others fixed. The plasma treatment had 4 different parameters (treatment duration, plasma power, chamber pressure, and plasma gas) to be tested for their effects on the surface response to the treatment. Design of experiments (DOE) was used since a designed experiment is a more effective way to determine the impact of two or more factors on a response than an OFAT experiment because,

- DOE requires fewer resources (experiments, time, material etc.) for the amount of information obtained. This was of major importance in the course of the project because significant characterization methods such as XPS had to be done outside the Sicomp facilities and DOE lowered costs and time significantly by lowering the number of samples.
- The estimates of the effects of each factor are more precise since using more observations to estimate an effect results in higher precision (reduced variability). This is because in DOE all the observations are used to estimate the effect of each factor and each interaction, while typically only two of the observations in OFAT experiment are used to estimate the effect of each factor. In the case of 4 factors, DOE came in very handy for making connections between the effects.
- The interaction between factors can be estimated systematically whereas in OFAT usually a hit-and-miss scattershot sequence of experiments are performed
- There is experimental information in a larger region of the factor space which improves the prediction of the response in the factor space by reducing the variability of the estimates of the response in the factor space, making the process optimization
more efficient since the optimal solution is searched for over the entire factor space. Considering that the goal in this project was to find the ideal plasma treatment parameters for the best results, estimations guided by the results obtained via DOE were very helpful.

2.5. Carbon Fiber Characterization Techniques

The region between the fibers and matrix, which contains unique micromechanical properties, is characteristically called the interphase and it influences the bulk composite properties to a great extent. Due to the small size of the interfacial region, its characterization can pose difficulties. Characterization methods for the interface can be divided into three main titles, which are macroscopic, mesoscopic, and microscopic characterization methods (Fig. 22). Macroscopic test methods mainly focus on the macroscopic composite, such as 3D fabric carbon fiber reinforced composites, 2D carbon fiber composite board et cetera. Mesoscopic interface test methods can be used for the carbon fiber bundle composites and single fiber composites. Microscopic characterization methods on the other hand focus on the micro fiber surface performance. These methods can be classified under more than one scale depending on how the characterization is performed and what the purpose of characterization is.

![Interfacial characterization methods for composites](image)

*Figure 22: Interfacial characterization methods for composites [58]*

Macroscopic test methods
- 90° tensile
- Off-axis tensile
- Notched impact
- NOL
- ILSS
- SEM

Mesoscopic interface test methods
- IPSS
- SEM
- AFM
- Wetting characterization

Microscopic experimental methods
- SEM
- AFM
- XPS
- Wetting characterization
2.5.1. **Scanning Electron Microscopy (SEM)**

Scanning electron microscopy will be used to observe and compare the effects of different surface treatments (acid and plasma) on the carbon fiber surfaces. These images will be used for qualitative analysis in order to support the findings on the effects of surface treatment methods on the mechanical properties of the carbon fibers. In addition, SEM will be used to measure and compare the fiber diameters before and after the treatment.

2.5.2. **X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS) will be used to analyze the chemical composition of the surface. This method will quantitatively analyze the chemical composition of the treated carbon fiber surfaces to detect and identify the attached surface groups. As the main purpose of the project is to enhance the interfacial adhesion between the fiber and the matrix, XPS results will be crucial in supporting the single fiber fragmentation findings. Amount of different elements are to be expressed in atomic % to compare the effects of different plasma types and parameters on the creation of surface groups.

2.5.3. **Contact Angle Measurements**

Contact angle measurements will be performed only on the lignin samples since it is a very cumbersome and time consuming process. The Wilhelmy method will be used to measure and compare the effects of different plasma gases on the adhesive properties of the carbon fibers. This data when combined with the XPS and fragmentation results will provide important information on the effects of surface treatment on fiber-matrix interface.

2.5.4. **Single Fiber Tensile Tests**

Tensile tests will be performed on the treated and untreated rayon and lignin samples in order to observe the effects of different treatment types on the tensile properties of the carbon fibers. Quantitative data from these experiments when combined with the supportive qualitative data from the SEM images will give a detailed picture of the effects of surface treatment on the carbon fiber samples.

2.5.5. **Single Fiber Fragmentation Tests (SFFT)**

Single fiber fragmentation (SFF) is a quantitative analysis method used to control the degree of adhesion on the microscale. The fragmentation test is developed from the early work of Kelly and Tyson, who investigated brittle tungsten fibers that broke into multiple segments in a copper matrix composite. At present, the single fiber fragmentation test is one of the most popular methods to evaluate the interface properties of fiber-matrix composites on the microscale. Each specimen consists of a single fiber embedded in a chosen matrix. Elongating the specimens under tensile stress leads to the fragmentation of fibers. The fiber inside the resin breaks into increasingly smaller fragments under tensile stress at locations where the fiber axial stress reaches its tensile strength. Naturally, this requires a resin system with a
sufficiently higher strain to failure than the fiber’s. When the fiber breaks, the tensile stress at the fracture location reduces to zero. Due to the constant shear in the matrix, the tensile stress in the fiber increases roughly linearly from its ends to a plateau in longer fragments. The higher the axial strain, the more fractures, and hence fragments, will be caused in the fiber, but at some level the number of fragments will become constant as the fragment length is too short to transfer enough stresses into the fiber to cause further breaking (Fig. 23).

Figure 23: Left: Specimen with increasing number of fiber breaks due to increased strain levels in the matrix. Right: Stress in fiber as a function of position for the respective matrix strain level. Zero stress corresponds to a position with a fiber break [59]

The average shear strength at the interface, whether bonded, debonded or if the surrounding matrix has yielded, whichever occurs first, can be estimated from a simple force balance equation for a constant interfacial shear stress:

$$\tau = \frac{\sigma_f(l_c)d}{2l_c}$$

(9)

Where $\sigma_f$ is the fiber strength at critical length, $d$ is the fiber diameter and $l_c$ is the critical fragment length of the fiber. In order to determine the interfacial shear stress, one needs to measure the average fragment length at the saturation stage, where no more breaks occur when applying further strain to the specimen.

$$l_c = \frac{4}{3 \# \text{ of fiber fragments}}$$

(10)

From this, calculation of the critical length and interfacial shear strength can be done. A stronger fiber-matrix bond results in a shorter critical fragment length due to the better stress transfer, which results in higher number of fragments. Moreover, the shape of the fiber breaks and the debonding features between fiber and matrix are characteristic for the composite
system. If the bonding at the interface is strong, the fiber cracks will propagate into the matrix and cause the matrix to deform around the crack (Fig.24). On the other hand, if the interface bonding is weak, debonding between fiber and matrix occurs and the fiber slips out. Both the breaking gap and the debonding zone will become wider with the matrix remaining entirely or almost entirely intact (Fig. 25).

Data processing of SFFT consists of the calculation of an interfacial adhesion parameter either from the distribution of fragment lengths using a force balance equation based on Kelly-Tyson model, or from the measurement of debonding length using energy balance schemes. Shape behavior of the SFFT plots can give important information regarding the fiber-matrix adhesion at the interface. Shape analysis records the matrix strain and the respective number of fiber breaks. For low strains, no fiber breaks will occur until the fiber failure strain is reached. After the first break, the frequency will increase and slow down again while reaching saturation hence yielding an S-shaped curve (Fig. 26).
Figure 26: Crack density versus applied strain for glass fibers and carbon fibers. Note that carbon fibers undergo fragmentation process earlier due to their more brittle nature compared to the glass fibers [59]

Furthermore, S-curves can shift in the x and/or y directions depending on the degree of the interfacial modification. A shift towards the positive x axis in the onset of fragmentation indicates weaker bonding, whereas a shift towards the positive y axis in the number of fragments can be interpreted as stronger interface bonding. This is especially useful in comparing the S-curves of untreated and surface treated samples in order to observe the difference in the interfacial behavior of both (Fig. 27).

Figure 27: S-curves for different types of surface treatments [59]
3. Experimental

3.1. Materials

Untreated, unsized, and undrawn lignin based carbon fibers (fiber diameter 11.1 ± 0.3 µm), which were produced via LignoBoost process for separation of lignin from black liquor, were obtained from Innventia AB (Stockholm, SE). Rayon based carbon fibers UVG-22-C (fiber diameter 8.5 ± 1.0 µm) to be used for comparison purposes, which were also untreated and unsized, were received from SvetlogorskKhimvolokno (Svetlogorsk, BY).

3.2. Surface Treatment Methods Employed

Lignin based and rayon based carbon fiber samples were treated in a TePla 440 (Technics Plasma GmbH, DE) microwave plasma chamber (Fig 28). Both rayon and lignin samples with the same treatment parameters were put inside the chamber and treated at the same time. Each sample consisted of a bundle of fibers taped on an aluminum foil on one end to keep the fibers from flying during the flushing of the chamber with gas, while the aluminum foil ensured conduction throughout the fibers. The fibers that make up the bundles were separated from each other prior to treatment via tweezers in order to prevent any possible shadowing effect that would block the plasma gas from reaching the fibers uniformly. To achieve results as reproducible as possible, all the samples were prepared and treated in the same fashion. After each parameter was changed, the chamber was flushed and evacuated with the selected treatment gas to prevent contamination in the chamber. Oxygen, nitrogen, air and propylene plasmas were created inside the chamber with varying parameters of treatment duration, chamber pressure, and plasma power. Throughout the course of the surface treatment, the treatment duration was varied between 2 seconds and 2 minutes, chamber pressure was varied between 0.7 mbar and 1.5 mbar, and plasma power was varied between 200 W and 400 W. Treated samples were stored and sealed in bags inside a glove box with argon atmosphere in order to prevent exposure of treated fibers to air (Table 2).

In order to provide samples for comparison with the conventional surface treatment methods, rayon and lignin based carbon fibers were surface treated with nitric acid (HNO₃). The samples were treated in 65 wt% nitric acid solution at 115° C. The treatment duration was varied between 15 and 60 minutes. Treated samples were washed thoroughly with distilled water prior to being dried in the oven at 100° C for 72 hours.
Table 2: Plasma treatment parameters for rayon and lignin fibers

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fiber Type</th>
<th>Plasma Gas</th>
<th>Treatment Time</th>
<th>Plasma Power (W)</th>
<th>Chamber Pressure (mbar)</th>
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<tr>
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<td>2 seconds</td>
<td>200</td>
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<td>200</td>
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<td>R9</td>
<td>Rayon</td>
<td>Air</td>
<td>1 minute</td>
<td>300</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Figure 28: Plasma chamber used for the surface treatment
3.3. Sample Preparation for Single Fiber Tensile Tests

For the single fiber tensile tests, 10 test samples were prepared for each specimen in order to get the adequate statistical parameters. Single fibers were separated and glued on a paper frame for length standardization purposes. This was an important step since the fiber tensile strength depends on the specimen length due to the flaws in the material, which statistically increases with the increasing sample length. A 2 cm sample length was chosen since it was very difficult to single out lignin fibers without breaking them, so the samples were kept at a mediocre length (Figure 29).

![Figure 29: Instron 4411 tensile tester with the pneumatic grips for single fiber tensile test (left) and the 20mm (cut-out length) frame used for the sample preparation (right)](image)

3.4. Sample Preparation for Single Fiber Fragmentation Tests

SFFT sample preparation is a multiple step process. At first single fibers were picked out and separated from bundles. Then these single fibers were put on a pulley mechanism with weights attached on both ends in order to pre-strain the fibers. Pre-straining the fiber before impregnation is of high importance since thermal residual stresses due to resin curing introduce compressive strains in the fiber, and thus the fiber must elongate more in order to break under tension. Therefore, the saturation limit for fiber breakage can often only be reached if fiber pre-straining compensates for these residual stresses. The system used in the pre-straining process was hand-made and it was tailored for the short and fragile lignin fibers (Fig. 30).
Following the pre-straining process using weights, the strained fibers are picked up using a U-shaped aluminum frame with double sided tape on it. Once the fiber ends are picked up by the tape, the weights are cut off and the fiber stays under strain until impregnation (Fig. 31).

Following the pre-straining process, the fibers are impregnated in epoxy resin. Araldite Ly5052 resin was mixed with Araldur 5052ch curing agent with a 100:38 mixing ratio. For the impregnation process, a custom made steel mold is used (Fig. 32). Once the aluminum frame with the pre-strained fibers is stabilized on the steel mold, the mold is assembled and the bolts are tightened in order to achieve uniform thickness on all sides. After making sure
the thickness is uniform on all sides, epoxy mix is poured into the mold slowly. When the mold is filled with epoxy, it is placed in the oven for the curing process (Fig. 32).

![Diagram of steel mold for fiber impregnation](image)

*Figure 32: Cross-section of the steel mold used for fiber impregnation*

When the epoxy is cured and the fibers are immobilized inside the cured epoxy, the mold is opened and fragmentation samples are cut using saw. It is important to keep the dimensions of the samples as uniform as possible since different size samples will behave differently and this will have an adverse effect on the reliability of the results.

Due to difficulties in obtaining long single fibers from the main batch, the U-shaped aluminum frame was scaled down, which yielded samples with dimensions smaller (110 mm x 5 mm x 2 mm) than those set for continuous production in previous studies.
4. Results and Discussion

4.1. Optical Microscopy (OM)

In order to observe the immediate effects of the surface treatment on the carbon fiber surface, optical microscopy was chosen since it is a relatively fast and cheap initial characterization method. Oxygen, air, and nitrogen plasma treated unsized lignin based carbon fibers were examined under the optical microscope to observe the changes on the fiber surface in response to different plasma treatments. It was noted that the surface topography was altered to some extent with the introduction of some level of surface roughness observable with an optical microscope (Fig. 33). This seemed puzzling since it was expected that the plasma treatment should have been somewhat easy on the fiber surface due to its low gas temperature and short exposure time. Especially the oxygen plasma treated sample had visible deformations on the surface. This observation was noted to be investigated further with scanning electron microscopy (SEM) later.

![Figure 33: From left to right in pairs; untreated CF, oxygen plasma treated CF, air plasma treated CF, and nitrogen plasma treated CF (lignin)](image-url)
4.2. Scanning Electron Microscopy (SEM)

The effect of the plasma treatment on the fiber surface morphology was observed using a scanning electron microscope (SEM). Due to the relatively good conductivity of carbon fibers no additional coating was applied to the fibers prior to SEM. However the lack of a coating on the fiber surface made the close examination of the surface difficult. The fibers were dipped in silver paint to ensure conductivity just in case. Initial observations of the untreated and plasma treated fibers were performed in Sicomp Mölndal facilities, whereas observations on the nitric acid treated fibers were done at LTU. The nitric acid treated samples were expected to exhibit a pronounced rise in surface roughness in the form of pits and grooves. In reality, the surface morphology difference between the acid treated and untreated fibers was rather subtle.

Surface of the untreated fibers was very smooth as expected (Fig. 34). This smooth appearance can be explained by the formation of large graphitic basal planes during the carbonization process. Different plasma treatment methods had similar effects on the surface morphology. Prior to plasma treatment, there were visible flakes on some of the fibers. These flakes were gone after a short treatment indicating the cleaning effects of the plasma treatment (Fig. 35).

Figure 34: Untreated lignin based CF surface under SEM
Effects of plasma treatment on the fiber surface morphology were not always visible. Prior to characterization, oxygen plasma was expected to have the most severe effects on the fiber surface. Moreover due to the high nitrogen content in air, air and nitrogen plasmas were
expected produce similar results. SEM images showed that oxygen and air plasmas did not have visible effects on the surface morphology (Fig. 36). Considering that plasma treatment introduces nano-scale surface roughness and is preferred specifically for that feature for it does not deter the tensile properties of the fiber, a visible increase in surface roughness was not expected anyway. On the other hand, nitrogen plasma treated lignin fibers exhibited a visible rise in surface roughness in the form of spots (Fig. 37).

Fiber diameters of the treated and untreated fibers were also of interest during the SEM observations. Since both acid and plasma treatments cause some sort of etching on the carbon fiber surfaces, diameter changes were expected on the treated fibers, especially for the acid treated samples. None of the plasma treated lignin samples showed a trend of change in their diameters as a result of the treatment, which was in accordance with the expectations. Due to the scarcity of the lignin based carbon fibers that were sent from Innventia AB, acid treatment was not performed on these samples for conservation reasons. Instead, acid treatment was performed on rayon based carbon fibers to compare and contrast its effects with the plasma treatment. Measured fiber diameter values before and after the plasma treatment shows no drastic changes not only between the untreated and treated samples but also among the different plasma treated samples (Fig. 38).
Rayon based fibers also exhibited similar results to those of lignin based fibers. Despite the expectations, a rough nitric acid treatment did not have any substantial reduction effects on the rayon fiber diameters. Nonetheless, this does not mean that acid treatment does not have any adversary effects on the mechanical properties of fibers since SEM gives only qualitative observational data and single fiber tensile tests will provide a comprehensive analysis on the effects of treatment methods on the mechanical properties of these fibers.

4.3. X-ray Photoelectron Spectroscopy (XPS)

XPS is a very surface sensitive method and it provides the surface chemical composition in atomic % for the outermost 2-10 nanometers of surfaces. The measuring principle is that a sample, placed in high vacuum, is irradiated with well-defined x-ray energy resulting in the emission of photoelectrons. Only those from the outermost surface layers reach the detector. By analyzing the kinetic energy of these photoelectrons, their binding energy can be calculated, thus giving their origin in relation to the element and the electron shell. XPS provides quantitative data on both the elemental composition and different chemical states of an element (different functional groups, chemical bonding, oxidation state, etc.). All elements except hydrogen and helium are detected, and the surface chemical composition obtained is expressed in atomic %.

XPS spectra were recorded using a Kratos AXIS UltraDLD x-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) at the SP Technical Research Institute in Stockholm, SE.
The samples were analyzed using a monochromatic Al x-ray source. The carbon fibers were of two types, based on rayon or lignin, with a thickness of each fiber (diameter) ca 10-11 micrometer therefore, a bunch of carbon fibers were mounted beside each other on the XPS sample holder, and then the analysis was conducted over an area area with most of the signal from an area of 700 x 300 micrometers. This means that the analysis data were obtained from several carbon fibers, and not from one single fiber.

The objective of XPS was to characterize the top nanometer surfaces of different carbon fiber samples as regards to the surface chemical composition. It was of interest to compare the samples, since different plasma treatments have been used. Therefore the interest to get the amount of different elements expressed in atomic%, and to check e.g. for if the samples have different degree of oxidation (before and after plasma treatment), etc (Table 3).

In high-resolved carbon spectra the three carbon peaks of main interest were C2-, C3- and C4-carbons. The possible changes in these peaks when compared with the XPS data from before and after the plasma treatment can give information about changes in the amount of different functional groups between C and O and N. The focus in comments to data in Table 4 will therefore be on the two largest peaks, C2- and C3-carbons.

High-resolution carbon spectra, with chemical shifts due to carbons in different functional groups with oxygen, have been grouped into four types of carbon peaks:

- **C1-carbon:** unoxidized carbon (C-C, C-H, C=C) between C1- and C2-carbon: C-N functional groups
- **C2-carbon:** carbon with one bond to oxygen (C-O, C=O-C)
- **C3-carbon:** carbon with two bonds to oxygen or nitrogen (C=O, O-C-O, N-C-O, N-C=O) if any possible Na-salts: R-COO- Na+
- **C4-carbon:** carbon with three bonds to oxygen (O-C=O, C(=O)OH, N-C(=O)-N)

The last C5-carbon peak in the curve-fit has only been included to fill out the gap provided due to the long slope, and this C5-carbon peak does not correspond to any functional groups. The results in Table 4-5 show that for all samples there are high amounts of unoxidized carbon (C1-carbon: C-C, C-H, C=C functional groups, such as found in hydrocarbon chains/aromatic groups) present, and of the total carbon peak this is between 63.0-81.5 % from C1-carbon functional groups. There is also some carbon with one bond to oxygen (C2-carbon), and of total carbon signal this is 7.3-16.8 % from C2-carbon functional groups. In addition there are some lower amounts of even more oxidized carbon peaks present with 3.1-11.1 % of total carbon as C3-carbon, and 2.5-5.1 % of total carbon as C4-carbon.
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<td>-</td>
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<td>-</td>
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<td>91.2</td>
<td>7.3</td>
<td>1.1</td>
<td>-</td>
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<tr>
<td>R8</td>
<td>87.3</td>
<td>11.3</td>
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<tr>
<td>R9</td>
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<td>0.1</td>
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<td>(&lt;0.05)</td>
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</tbody>
</table>

- = signal in detail spectra at noise level (below about 0.05-0.1 atomic %)

( ) = weak peak, signal close to noise level

Table 3: Relative surface composition in atomic %

For lignin based fibers the largest changes in the surface chemistry are observed for samples L2, L4, L6, L8 and L9, compared to untreated ref. sample L0. The effect was observed in both the total amounts of O and N and the atomic ratios O/C in Table 3, and the different functional groups in Tables 4-5. Note especially changes in C2-carbons (e.g. C-O, C=O-C functional groups), and to some extent also C3-carbons (e.g. C=O, O-C-O, N-C-O, N-C=O functional...
groups). The data in Table 4 corresponds to the relative distribution for different carbon peaks that could be observed under the high-resolved spectra, where the C2-carbon peak at ca 286.7 eV is easiest to detect the increase in area for L2, L4, L6, L8 and L9 samples compared to the untreated ref. sample L0.

<table>
<thead>
<tr>
<th></th>
<th>L0</th>
<th>&lt;</th>
<th>L2, L4, L6, L8, L9</th>
</tr>
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<tbody>
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<td>15.5 - 20.4</td>
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<tr>
<td>N tot (atomic %):</td>
<td>0 &lt;</td>
<td>0.7 - 1.5</td>
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<tr>
<td>C2-carbon (atomic %):</td>
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<td>9.7 – 12.4</td>
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<td>C3-carbon (atomic %):</td>
<td>4.1 &lt;</td>
<td>6.9 – 8.3</td>
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</tr>
</tbody>
</table>

For the rest of the samples (L1, L3, L5 and L7) the XPS data are found in between the above values. Note however that all samples have higher values than the reference sample L0.

For rayon based fibers the largest changes in surface chemistry are observed for samples R2, R4 and R8, and to some extent also samples R6 and R9, compared to untreated ref. sample R0. The effect was observed in both the total amounts of O and N and the atomic ratios O/C in Table 3, and the different functional groups in Tables 4-5. Note especially changes in C2-carbons (e.g. C-O, C=O-C functional groups), and to some extent also C3-carbons (e.g. C=O, O-C-O, N-C-O, N-C=O functional groups). The data in Table 4 corresponds to the relative distribution for different carbon peaks we can observe in the high-resolved spectra, where the C2-carbon peak at ca 286.7 eV is easiest to detect the increase in area for R2, R4 and R8 samples, and also R6 and R9 samples, compared to the untreated ref. sample R0.

<table>
<thead>
<tr>
<th></th>
<th>R0</th>
<th>&lt;</th>
<th>R6 and R9</th>
<th>&lt;</th>
<th>R2, R4 and R8</th>
</tr>
</thead>
<tbody>
<tr>
<td>O tot (atomic %):</td>
<td>0.8 &lt;</td>
<td>7.6 – 8.3 &lt;</td>
<td>11.3 – 13.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N tot (atomic %):</td>
<td>0 &lt;</td>
<td>0.5 – 0.7 &lt;</td>
<td>1.0 – 2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O/C atomic ratio:</td>
<td>0.01 &lt;</td>
<td>0.08 – 0.09 &lt;</td>
<td>0.13 – 0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2-carbon (atomic %):</td>
<td>7.2 &lt;</td>
<td>11.4 – 12.0 &lt;</td>
<td>13.0 – 14.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3-carbon (atomic %):</td>
<td>3.1 &lt;</td>
<td>4.4 – 4.5 &lt;</td>
<td>4.6 – 6.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the rest of the samples (R1, R3, R5 and R7) the data are mainly found in between the above values. Note however that all samples have slightly higher values than the reference sample R0.
### Table 4: Chemical shifts in the high-resolution carbon spectra, with the binding energy positions for each carbon peak after adjusting C1-carbon peak to 284.4 eV as the reference value. The chemical shifts in C2-, C3- and C4-carbon peaks are due to carbons in different functional groups with oxygen mainly, but also to some nitrogen. The last C5-carbon peak has only been included to fill out the gap provided due to the long slope, and this C5-carbon peak do not correspond to any functional groups.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic%</th>
<th>C tot</th>
<th>C 1</th>
<th>C 2</th>
<th>C 3</th>
<th>C 4</th>
<th>C 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L0</td>
<td>93.1</td>
<td>74.8</td>
<td>6.8</td>
<td>4.1</td>
<td>2.8</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>L1</td>
<td>82.4</td>
<td>59.6</td>
<td>9.0</td>
<td>5.9</td>
<td>3.7</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>L2</td>
<td>76.2</td>
<td>50.8</td>
<td>11.2</td>
<td>7.8</td>
<td>3.3</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>L3</td>
<td>82.2</td>
<td>60.5</td>
<td>8.2</td>
<td>5.7</td>
<td>4.2</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>L4</td>
<td>76.7</td>
<td>51.6</td>
<td>9.7</td>
<td>8.3</td>
<td>3.6</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>L5</td>
<td>83.9</td>
<td>62.0</td>
<td>7.9</td>
<td>5.7</td>
<td>4.0</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>L6</td>
<td>78.8</td>
<td>53.3</td>
<td>9.9</td>
<td>8.0</td>
<td>3.5</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>L7</td>
<td>87.1</td>
<td>67.4</td>
<td>7.7</td>
<td>4.9</td>
<td>3.6</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>L8</td>
<td>73.9</td>
<td>46.6</td>
<td>12.4</td>
<td>8.2</td>
<td>3.6</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>L9</td>
<td>75.2</td>
<td>51.4</td>
<td>10.1</td>
<td>6.9</td>
<td>3.3</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Rayon:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R0</td>
<td>99.0</td>
<td>80.7</td>
<td>7.2</td>
<td>3.1</td>
<td>2.5</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>95.2</td>
<td>75.7</td>
<td>7.9</td>
<td>3.7</td>
<td>2.7</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>85.7</td>
<td>59.4</td>
<td>14.0</td>
<td>5.3</td>
<td>2.9</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>91.2</td>
<td>68.1</td>
<td>9.9</td>
<td>4.5</td>
<td>3.5</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>83.8</td>
<td>57.8</td>
<td>13.0</td>
<td>6.3</td>
<td>3.4</td>
<td>3.3</td>
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<tr>
<td>R5</td>
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<td>71.8</td>
<td>8.9</td>
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<td>68.4</td>
<td>11.4</td>
<td>4.4</td>
<td>2.6</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>R7</td>
<td>91.8</td>
<td>70.5</td>
<td>8.2</td>
<td>4.7</td>
<td>3.5</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>R8</td>
<td>87.3</td>
<td>62.0</td>
<td>14.2</td>
<td>4.6</td>
<td>2.8</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>R9</td>
<td>90.8</td>
<td>66.2</td>
<td>12.0</td>
<td>4.5</td>
<td>3.0</td>
<td>5.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 5: The table shows the total amount of carbon (in atomic%) divided into the different carbon peaks. Values were calculated from data in Tables 1b and 2b, using two decimals from the raw data. Chemical shifts in the high-resolution carbon spectra, with the binding energy positions for each carbon peak after adjusting C1-carbon peak to 284.4 eV as the reference value. The chemical shifts in C2-, C3- and C4-carbon peaks are due to carbons in different functional groups with oxygen mainly, but also to some nitrogen. The last C5-carbon peak has only been included to fill out the gap provided due to the long slope, and this C5-carbon peak does not correspond to any functional groups.
The XPS results were analyzed using Modde® design of experiments analysis software by µmetrics. The factors and responses were entered into the software in order to investigate their effects on the creation of surface groups. The results were fitted using Partial Least Squares (PLS) method instead of Multiple Linear Regression (MLR) since PLS yielded a better model with a higher summary of fit looking at the higher R2 and Q2 values. The factors (treatment time, plasma power, chamber pressure, gas type) were investigated for their effects on the responses such as O/C ratio and C2-C3-C4 atomic percentages. In order to make a quantitative analysis possible with the software, gas type was quantified in terms of O content for oxygen, nitrogen and air. Oxygen plasma gas was given a value of 1 for the O content factor whereas nitrogen plasma was given a value of 0 for the O content, which made air, as the mix of these two gases, the middle value. Another important aspect in the XPS analysis was that the data in Table 5 show the amount in each carbon peak expressed in atomic %, instead of the relative values in Table 4. These absolute values expressed in atomic % are sometimes better to use instead of the relative values, for example in times when the total amount of carbon varies between samples as it does in the case here. For this reason, during the analysis of XPS results, C2-C3-C4 data was taken from Table 5 instead of Table 4.

For lignin samples O/C ratio, C2 and C3 atomic percentages were fitted well to the PLS fit model with rather high values of R2 and Q2 whereas C4 was a not that good of a fit for the report, so any correlation detected with regards to C4 should be reinvestigated with a larger sample pool (Figure 39).

The effect of each treatment parameter on the creation of surface groups was analyzed and some interesting results were obtained. Treatment time had the largest effect on the creation of surface groups for all responses with a good fit (O/C, C2, and C3). Treatment time had a positive effect on the creation of surface groups and the interaction between the factor and the response was directly proportional. This was in accordance with the expectations as the increased treatment duration means more functionalization will occur at the surface for a given area. O/C ratio was of primary interest here and it had a rather large positive coefficient for treatment time indicating a directly proportional relationship. C2 (C with one bond to oxygen) and C3 (C with two bonds to oxygen) showed similar trends for increased treatment time and exhibited a directly proportional relationship. The inversely proportional relationship between the C4 (C with three bonds to oxygen) was thought to be due to peeling of the surface layer and the related cleavage of the basal plain to host smaller and less stable oxygenated groups with the increased exposure to plasma energy (Figure 40). On the other hand, C3 and C4 values are much lower compared to C2 therefore their trends are less reliable than that of C2’s.
Figure 39: Summary of fit for the PLS fit method used to analyze the effects of treatment parameters on the creation of surface groups on lignin based carbon fibers.

Figure 40: Effects of different treatment parameters (treatment time, plasma power, chamber pressure, gas type) on the creation of surface groups (O/C, C2, C3, C4) on lignin based carbon fibers with respect to each other. A positive coefficient indicates a directly proportional relationship between the factor and the response whereas a negative coefficient indicates an inverse relationship.
During plasma oxidation of a surface, the sample is usually negatively biased with respect to the plasma by means of an external power source, so positive ions play a very significant role in plasma-surface interactions. Ions bring energy to the surface and therefore can assist in reactions of volatile species or induce direct sputtering. In a plasma etching system, sample bias is more or less expressed in ion energy, which is a function of the plasma power applied to sustain the discharge and chamber pressure, therefore it is safe to say that the ion flux and ion energy are not independent parameters. The limiting condition in a plasma etching system is that it needs to operate at low pressure and simultaneously achieve a high plasma density and low impact energy at the sample surface. The reason for this is because the ions play a fundamental role as the whole plasma process is essentially a directional ion bombardment to the sample surface. Assuming that the sample is the primary and ultimate target for these ions, achieving direct bombardment onto the sample depends on having no collisions for the ions on their travel from plasma to the sample surface. Efficiency of the plasma bombardment therefore depends heavily on plasma density and chamber pressure. Indeed, as it can be seen from the negative coefficient of pressure on the creation of the surface groups during plasma etching, low chamber pressure is desired to increase ion bombardment efficiency and achieve a uniform and anisotropic etching (Figure 40). At high pressure, the ions start colliding with each other and chamber walls before they reach the sample and therefore lose the energy they need for etching and functionalizing the sample surface. For this reason, high plasma density is necessary to keep production rate of active species and plasma etching at high levels, hence a high input power and low chamber pressure are important conditions. On the other hand, previous studies indicate that extremely low gas pressures (P≈0 mbar) also lead to inefficient plasma modification due to the number of ionized species being too small in the chamber because gas pressure effectively means the amount of ionizable material inside the chamber. This shows that rather than an overall directly or inversely proportional relationship between the chamber pressure and the creation of surface groups, there is actually an ideal spot where the positive pressure effects are maximized and the negative effects are minimized. A lower pressure range could be investigated for further studies in order to observe full behavior of functionalization with respect to chamber pressure.

Plasma power did not have that pronounced of an effect on the O/C ratio and detection of C2 and C3 carbons when compared to treatment time considering that its coefficient was approximately 1/8 of that of the coefficient for treatment time. The main reason for this low effect was thought to be because of the power range chosen for the experiment (200 W – 400 W) was already in the higher portion of the spectrum since in the literature there were plasma oxidation experiments conducted at levels almost 4 times less (50 W) than the minimum power value chosen for this investigation (200 W). Therefore the effect of plasma power on the creation of surface group was observed in the plateau region with not much effect. For
future experiments, the plasma power range can be lowered in order to observe the effects better. Concerning this study though, for the sake of lowering cost of production, plasma power can be kept as low as possible within the 200 W – 400 W range along with a low chamber pressure as indicated by results. The only plasma power effect worth noting in the 200 – 400 W range was on C4, which was thought to be due to the higher energy needed to form bulkier bonds (double or triple) since the plasma power was observed to be directly proportional with the creation and detection of these bonds.

As it was mentioned earlier, in order to make a quantitative analysis possible with the software, gas type used was quantified in terms of O content for oxygen, nitrogen and air. Oxygen plasma gas was given a value of 1 for the O content factor whereas nitrogen plasma was given a value of 0 for the O content, which made air, as the mix of these two gases, the middle value needed for the analysis. Plasma gas type had an observable effect on the creation of surface groups. It can be seen that oxygen content has a positive effect on the creation surface groups and it is directly proportional with the level of functionalization. In other words, oxygen plasma leads to a more efficient functionalization of the carbon fiber surface compared to nitrogen plasma (Figure 40). Since chemical species inside the chamber play a very important role in the plasma etching process, it is no surprise that the type and amount of different surface groups created, differ with plasma gas type. One thing to note is the amount of nitrogen and oxygen groups present before and after the treatment. The amounts of oxygen detected on the surfaces of each sample were approximately an order of magnitude larger than those of nitrogen detected (Figure 40). Even for the samples that were treated only with nitrogen plasma, oxygen content was still much higher. Looking at the results it can be seen that more oxygen functionalization takes place compared to nitrogen functionalization for the same treatment parameters. One of the reasons for the high values of oxygen functions in the nitrogen treated samples could be the presence of oxygen on the untreated samples. The oxygen already present on the surface of the untreated fibers are activated with plasma energy, regardless of the type of gas used, and therefore are not only observed as a rise in O/C ratio but also in C2, C3 and C4 levels since they bind to C atoms in different manners. ON the other hand, the behavior of nitrogen presence is similar to that of oxygen’s, which means that the parameters controlling the creation of these two groups are very similar if not the same. The main difference is in their amounts, which plays a significant role here therefore it is safe to say that oxygen plasma achieves better functionalization of the surface as a whole. The difference in the amount of functionalization can also be explained by differences in electronegativity values. Electronegativity value of oxygen is higher than the electronegativity value of nitrogen by a factor of 1.2 and this seemingly small difference can very well be magnified in the process of plasma etching and the resulting creation of surface groups.
With all the effects of different plasma parameters combined, a 4-D response contour was obtained in order to get a better idea of the combination of these effects for ideal plasma treatment parameters that would maximize the creation of oxygenated functions on lignin based carbon fiber samples (Figure 41).

![4D Response Contour of O/C and its dependence on the 4 different plasma treatment parameters for lignin based carbon fibers](image)

**Figure 41:** 4-D response contour of O/C and its dependence on the 4 different plasma treatment parameters for lignin based carbon fibers

As it can be clearly seen in the response contour of O/C, the best response for the amount of oxygen functions created on the carbon fiber surface is obtained with high power, high treatment time, low pressure and high oxygen content (oxygen plasma). The contour curves being linear and the lack of curvature indicates that the interaction term is not very significant meaning that the interactions between parameters are not very strong for a synergetic behavior (Figure 41).

From the XPS data it seems that the changes in surface chemistry are larger after plasma treatment of the lignin fibers when compared to the plasma treatment of the rayon fibers. Furthermore, it can be said that the largest changes in the surface chemistry are obtained with 2 min plasma treated specimens. Summary of fit plot for the rayon based samples also indicate a good model for the analysis of rayon based samples, which supports the reliability of the conclusions drawn from these results (Figure 42).
Figure 42: Summary of fit for the PLS fit method used to analyze the effects of treatment parameters on the creation of surface groups on rayon based carbon fibers.

Figure 43: Effects of different treatment parameters (treatment time, plasma power, chamber pressure, gas type) on the creation of surface groups (O/C, C2, C3, C4) on rayon based carbon fibers with respect to each other. A positive coefficient indicates a directly proportional relationship between the factor and the response whereas a negative coefficient indicates an inverse relationship.
The results obtained from the coefficients plot for the rayon samples show that responses and their significance coefficients correlate for the lignin based carbon fibers and rayon based reference carbon fibers (Figure 43). This feature supports the reliability of conclusions drawn for lignin cased carbon fibers while it points at a certain level of reproducibility. As expected, the 4-D response contour of O/C for the rayon based carbon fibers also behave in a similar manner to that of lignin based fibers’ (Figure 44).

Figure 44: 4-D response contour of O/C and its dependence on the 4 different plasma treatment parameters for rayon based carbon fibers

Aside from the investigation of the effects of plasma treatment parameters on the creation of surface functional groups, some very interesting observations were also made during the XPS analysis. For lignin based carbon fiber samples, traces of Sodium (Na) and Sulfur (S) elements were detected (Table 3). It is already known that the kraft process entails treatment of woodchips with a hot mixture of water, sodium hydroxide, and sodium sulfide in order to break the bonds that link lignin, hemicellulose and cellulose. On the other hand, all of the residues and impurities are usually carbonized during the carbonization process. Therefore, this seemingly insignificant observation actually provides valuable information on the state of the carbon fibers. Since, Na and S should have not been present on the carbon fibers that were adequately and sufficiently carbonized, the detection of these elements indicate insufficient carbonization of lignin based carbon fibers. Furthermore, these detections were not made for the commercial rayon based carbon fiber samples that were used as the reference, which rules out the possibility of contamination since they went through the same exact process from
plasma treatment to XPS analysis. This finding became even more important following the single fiber tensile tests, which will be mentioned further under that section.

4.4. Contact Angle Measurements

Contact angle measurements were performed on the lignin based carbon fibers with the Wilhelmy method. The Wilhelmy balance method is a widely used technique that indirectly measures contact angle on a solid surface. When a thin, smooth, vertical plate is brought in contact with a liquid, the change in its weight is recorded by a balance. The detected force change on the balance is a combination of buoyancy and the force of wetting (the force of gravity stays the same). As the solid sample is pushed into and pulled out of the liquid, and advancing or receding contact angle can be established, respectively (Figure 45).

Figure 45: A submersion cycle for the Wilhelmy balance measurement (1) Sample approaches the liquid (2) Sample is in contact with the liquid (3) Sample is immersed further and increased buoyancy lowers the force detected further (4) Sample is pulled out

3-5 fibers from each sample were put on a tape and contact angle values were measured 3 times for each fiber. Due to the cumbersome nature of the process, only lignin based fibers were characterized. The primary purpose of the contact angle measurements was to get a comparative perspective on the reduction of contact angle values with respect to different plasma gases used during the plasma etching process. All samples used in the contact angle measurements were plasma treated in the same vacuum chamber with 300 W plasma power, 0.7 mbar chamber pressure and 2 seconds treatment time. Three different plasma gases were tested and they were compared to the contact angle values of the untreated samples (Figure 46).
While the contact angle values were very high for untreated fibers, a drastic drop in the contact angles can be observed following a very short treatment of 2 seconds. Although small differences can be observed, since they are all in the error range it can be assumed that the effects of different gases on the contact angle values of lignin based carbon fibers are almost identical. Whether there would be a difference worth noting in terms of contact angle with an increased treatment duration could be investigated in the future but at short treatment times such as 2 seconds, all three gases achieve a drop of approximately 55% in terms of contact angle values.

### 4.5. Single Fiber Tensile Tests

Single Fiber Tensile Tests (SFTT) were conducted on the treated and untreated fibers in order to observe the effects of plasma treatment on the mechanical properties of the lignin based carbon fibers. SFTTs were performed on an Instron 4411 tensile machine using pneumatic grips (Figure 47). 20 mm samples with an average diameter of 11.1 µm were tested at a strain rate of 1% at 20.5°C and 25% relative humidity and data was collected as a force vs extension plot with 50 ms signal intervals.
10 fibers were picked from each sample and they were tested individually in order to achieve a good statistical distribution of the ultimate strength and Young’s modulus values. Young’s modulus calculations were made for the interval of 0.1% to 0.4% strain values in order to ensure that the calculations were made in the elastic region. There was not any parameter specific trends for the mechanical properties of the treated fibers therefore DOE analysis software was not used for the interpretation of results. A sample legend for easy identification of the samples is included below (Table 6). A compliance analysis for the tensile machine along with a Weibull analysis of the measurements can be found in Appendix 6.1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fiber Type</th>
<th>Plasma Gas</th>
<th>Treatment Time</th>
<th>Plasma Power (W)</th>
<th>Chamber Pressure (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L0</td>
<td>Lignin</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>L1</td>
<td>Lignin</td>
<td>Nitrogen</td>
<td>2 seconds</td>
<td>200</td>
<td>0.7</td>
</tr>
<tr>
<td>L2</td>
<td>Lignin</td>
<td>Oxygen</td>
<td>2 minutes</td>
<td>200</td>
<td>0.7</td>
</tr>
<tr>
<td>L3</td>
<td>Lignin</td>
<td>Oxygen</td>
<td>2 seconds</td>
<td>400</td>
<td>0.7</td>
</tr>
<tr>
<td>L4</td>
<td>Lignin</td>
<td>Nitrogen</td>
<td>2 minutes</td>
<td>400</td>
<td>0.7</td>
</tr>
<tr>
<td>L5</td>
<td>Lignin</td>
<td>Oxygen</td>
<td>2 seconds</td>
<td>200</td>
<td>1.5</td>
</tr>
<tr>
<td>L6</td>
<td>Lignin</td>
<td>Nitrogen</td>
<td>2 minutes</td>
<td>200</td>
<td>1.5</td>
</tr>
<tr>
<td>L7</td>
<td>Lignin</td>
<td>Nitrogen</td>
<td>2 seconds</td>
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<td>300</td>
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</table>

Table 6: Sample identification codes and their respective treatment parameters
Modulus values were calculated for each fiber and they were averaged for the overall sample. Extra samples were made due to the difficult nature of the sample loading process and prematurely broken samples were excluded from the analysis (Figure 48). Modulus values of the treated lignin fibers had an average of 7.2 GPa with a maximum of 8.4 GPa (L1) and a minimum of 6.3 GPa (L2). The untreated samples had a modulus of 6.8 GPa. The average coefficient of variation for the measurements was approximately 9%. As mentioned earlier, the modulus values calculated were very similar, indicating that there is not much difference among the fibers, therefore it was possible to compare their ultimate strength values without the interference of other factors such as different modulus values. Since the lignin based carbon fibers were still at development stage and not commercialized yet, a certain amount of variance was expected among the fibers but at least for modulus this difference was not really pronounced (Figure 48).

Tensile strength values were calculated for each fiber and they were averaged for the overall sample. Extra samples were made due to the difficult nature of the sample loading process and prematurely broken samples were excluded from the analysis (Figure 49). Weibull analysis was performed on untreated samples for which the details can be found in the Appendix 6.2. The untreated samples had a tensile strength of 152 MPa which exactly matched the strength value calculated using Weibull statistics. Alpha and Beta coefficients were 7.76 and 162 MPa respectively (Fig. 50). Considering that the shape parameter of carbon fiber ranges from 4 to 10, a value of 7.76 obtained from the experimental data seems

Figure 48: Average stiffness values of untreated lignin fibers (L0) and lignin fibers plasma treated with different treatment parameters
credible. Experimental values were in coherence with the values predicted by Weibull analysis (Fig. 51). The average coefficient of variation for the measurements was approximately 7%. Strength values of the treated lignin fibers had an average of 179 MPa with a maximum of 197 MPa (L1) and a minimum of 137 MPa (L8). The raw data in the form of force-displacement was processed into a stress-strain curve and the results were averaged for each sample. Before starting the experiments, it was expected from the findings in the literature that plasma treatment would not have any adversary effects on the strength values of the fibers like the acidic treatment would have with nitric acid. The results were in accordance with the expectations and no substantial decrease in the ultimate strength of the treated fibers was observed. In fact, for most plasma treated fiber samples there was a subtle increase in the tensile strength rather than a decrease. This could be attributed to the cleaning effect of the plasma treatment that was mentioned in the visual observations conducted via SEM. It is likely that the plasma treatment removes possible crack initiators on the surface by basically polishing the fiber surface and hence lowering and delaying the chances of crack initiation and the crack’s eventual propagation to failure. It is known that plasma treatment makes the surface smoother by removing existing flakes and flattening the surface as opposed to nitric acid treatment, which usually incorporates grooves onto the surface in order to enhance mechanical interlocking. Since, chemical interactions play a much more significant role in terms of adhesion than mechanical interactions do at the interface, preventing mechanical degradation at the expense of mechanical interlocking for a similar chemical effect is a profitable trade-off.

![Average Strength Values of Treated Fibers](image)

Figure 49: Average tensile strength values of untreated lignin fibers (L0) and lignin fibers plasma treated with different treatment parameters
During the mechanical tests, it was noticed that the stiffness and strength values of the lignin based carbon fibers were very low compared to the values reported in the literature (180 MPa, 7.2 GPa). Nordström et al. [60] reported an average tensile strength of 300 MPa with an average elastic modulus 30 GPa for softwood lignin based carbon fibers. The reason for this large deviation in mechanical properties was attributed to insufficient carbonization of the softwood lignin based carbon fibers during processing. This theory was also supported by detection of Na and S elements, presumably residual amounts from the kraft process, via
XPS. Combination of these two results along with a relatively lower density value for the lignin based carbon fibers compared to its counterparts indicate that the lignin based carbon fibers used in this study were insufficiently carbonized and that they exhibit polymer properties rather than carbon fiber behavior.

4.6. Single Fiber Fragmentation Tests

Single Fiber Fragmentation Tests (SFFT) were to be conducted as the final assessment method of the interfacial performance of lignin fibers treated with different treatment parameters. Plasma treated samples were embedded in epoxy resin and were cut out accordingly for fragmentation tests. However, due to a combination of technical, logistical and health related problems; the SFFTs were not successful and no meaningful data or observation was obtained. Nonetheless, the combination of contact angle measurements and XPS analysis provided valuable information regarding the creation of surface groups and their effects on the fiber/matrix adhesion.
5. Conclusions

Plasma treatment of softwood lignin based carbon fibers was performed in order to increase the interfacial adhesion between the fiber and the matrix by incorporating functional groups onto the fiber surface. Plasma treatment time, plasma power, chamber pressure and plasma gas type were varied in order to investigate their effects on the functionalization of the surface by various visual, chemical and mechanical characterization methods.

Observations with optical and scanning electron microscopies showed the cleaning effects of plasma treatment on the fiber surface by removal of flakes and smoothing of the fiber surface. The smoothing effect of plasma treatment was later supported by the subtle increase in the tensile strength of the plasma treated fibers and this was attributed to the elimination of crack initiators on the surface by a “polishing” effect. Modulus values were similar for all fibers. Contact angle measurements of the lignin based fibers showed that all plasma gases achieve a certain level of decrease in the contact angle values thus lowering the surface tension. X-ray photoelectron spectroscopy (XPS) results were analyzed using a design of experiments software with a PLS fit. For the highest amount of surface functionality to be achieved, it was concluded that oxygen plasma should be used with high plasma power, low pressure and a high treatment time. Since the ranges selected for parameters were mostly on the higher side, the trends were able to be predicted however pinning a point for an absolute sweet spot was not possible with the rather low amount of samples. Detection of Na and S elements combined with very low mechanical properties for all lignin based carbon fibers indicated insufficient carbonization of the softwood lignin based carbon fibers used in this study. Although this did not have an effect on the investigation of plasma treatment parameters on the creation of surface groups, it still is a feature that should be noted for further studies regarding the making of the carbon fibers.

Although SFFT would be the ultimate method to verify the results obtained from this study, XPS studies combined with contact angle measurements give strong indications about the behavior of surface functionality with respect to treatment parameters. Furthermore, visual observations along with mechanical tests support the notion that plasma treatment is a safe and useful method for improving fiber/matrix adhesion by the incorporation of surface groups onto the fiber surface.
6. Appendix

6.1. Machine Compliance Analysis

The stiffness values of lignin based carbon fibers with different lengths (10, 20, 50 mm) were obtained from additional tensile tests and machine compliance for Instron 4411 was calculated according to Eq. A1

\[ C = \frac{L}{EA} \]  

(A1)

Where C is compliance, L is the fiber length, E is the measured fiber stiffness (before the correction is applied) and A is the cross-sectional area of the fiber.

**Figure A1:** Compliance vs fiber length plot for the compliance analysis where offset compliance was calculated. Linear fit of the plot shown in the y=mx+b form, where b is the calculated offset compliance value.

The offset compliance (ΔC) was obtained from the equation of linear fit in the compliance vs fiber length plot. In this case, the value was equal to -0.0004 m/N. Following these calculations, the true compliance was calculated as

\[ C_{true} = C - \Delta C \]  

(A2)

Finally the corrected stiffness values were calculated by factoring the compliance in

\[ E_{true} = \frac{L}{C_{true}A} \]  

(A3)

Even though the compliance analysis for the machine was performed, the corrections were not used for the actual data since the calculated compliance turned out to be negative in this case.
6.2. Weibull Analysis

Strength of brittle materials like carbon fibers can be expressed with Weibull statistical distribution.

\[ P = 1 - e^{\frac{V}{V_0}(\frac{\sigma}{\beta})^\alpha} \]  \hspace{1cm} \text{(B1)}

Where \( P \) is probability of failure, \( \sigma \) is stress, \( V \) and \( V_0 \) volume of the sample and reference volume respectively, \( \alpha \) and \( \beta \) are shape and scale parameters.

Assuming constant cross-sectional area for the sample, \( V \) can be expressed in length.

\[ P = 1 - e^{\frac{L}{L_0}(\frac{\sigma}{\beta})^\alpha} \]  \hspace{1cm} \text{(B2)}

Where \( L \) is the fiber length and \( L_0 \) is the reference length.

Average strength \(<\sigma>\) can be calculated using the following formula.

\[ <\sigma> = \beta \left( \frac{L}{L_0} \right)^{-\frac{1}{\alpha}} \Gamma \left( 1 + \frac{1}{\alpha} \right) \]  \hspace{1cm} \text{(B3)}

These values that are described here can also be obtained experimentally by plotting probability of failure in Weibull coordinates. A linear fit approximation of the data points is used in order to calculate the scale and shape parameters (Fig. B1, B2)

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**Figure B1:** Determination of Weibull parameters for \( L_0 \) fibers by fitting experimental data to the Weibull model

\[ y = 7.7582x - 39.45 \]

\[ R^2 = 0.9358 \]

\( \alpha = 7.76 \)

\( \beta = 162 \text{ MPa} \)
Figure B2: Weibull model predicted values vs experimental data points

\[
\begin{align*}
\alpha &= 7.76 \\
\beta &= 162 \text{ MPa} \\
<\sigma> \text{ theor} &= 152 \text{ MPa} \\
<\sigma> \text{ exp} &= 152 \text{ MPa}
\end{align*}
\]
7. References


71


