Viability Study for a Carbon-Cork Sandwich Composite

Ivo Daniel Sampaio Giraldo do Rosário

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Supervisors: Prof. Pedro Miguel Gomes Abrunhosa Amaral
Prof. Ana Clara Lopes Marques

Examination Committee

Chairperson: Filipe Szolnoky Ramos Pinto Cunha
Supervisor: Pedro Miguel Gomes Abrunhosa Amaral
Member of the Committee: Paulo Miguel Nogueira Peças

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To everyone who keeps supporting me no matter what

iv

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Abstract

The present dissertation aims at analyzing the current reality of the composite industry in the aeronautics field while studying the development of a new sandwich composite material made of a cork agglomerate core and CFRP sheets. The continuous search in the aeronautics field for new lightweight materials with up to standards performance makes of cork and carbon fiber a logical choice for the development of a new composite material. This document covers the design and manufacturing phase, the testing and quality control and its economical and environmental impact. The combination of both materials looks very promising in addressing the product requirements for achieving a competitive production cost mainly due to the reasonable price of cork agglomerates. This new composite would also effectively reduce the carbon footprint of the aeronautics industry given the reduced environmental impact of cork and the new possibilities for carbon fiber recycling.

Keywords: cork, carbon fiber, sandwich composite, composite design, inner fuselage

Resumo

A presente dissertação pretende analisar a realidade atual da indústria dos materiais compósitos no setor aeronáutico, estudando o desenvolvimento de um novo material compósito sanduíche constituído por uma matriz de aglomerado de cortiça e folhas de fibras de carbono embebidas em resina. A procura contínua do setor por novos materiais mais leves com propriedades e comportamento adequados faz da cortiça e das fibras de carbono uma escolha lógica para o desenvolvimento de um novo material. Este documento cobre a fase de design e manufatura, a fase de testes e controlo de qualidade, bem como a análise do custo e do impacto ambiental. A combinação dos dois materiais aparenta ser promissora em responder aos requisitos do produto, com um custo de produção competitivo particularmente pelo preço mais razoável dos aglomerados de cortiça. Este novo material compósito também contribuiria para a redução da pegada de carbono da indústria aeronáutica dado o impacto ambiental reduzido da cortiça e as novas possibilidades de reciclagem de fibras de carbono.

Palavras-chave: cortiça, fibras de carbono, compósitos sanduíche, design de compósitos, fuselagem interna

x

Contents

List of Tables

List of Figures

Glossary

FEA: Finite Element Analysis

CFRP: Carbon Fiber Reinforced Polymer

MRP: Material Requirements Planning

PMI: Polymethacrylimide

SWOT: Strengths, weaknesses, opportunities and threats

PAN: Polyacrylonitrile

AN: Acrylonitrile

FAI: Flexure after impact

CAI: Compression after impact

VARI: Vacuum Assisted Resin Injection

SPC: Statistical Process Control

JAR: Joint Aviation Requirements

Chapter 1

Introduction

1.1 Scope and Objectives

Composite materials are becoming one of the most sought after solutions in a number of fields from aerospace to automotive, from construction to architecture. A composite material is made from two or more different materials with different properties that are combined in order to create a new material. Even though the physical and chemical properties of the different materials remain distinct in the new composite, these constituent materials work symbiotically to get improved properties in the final component, when compared to the original properties of each individual material.

Research in the aeronautics industry regarding composite materials has been extensive and continuous, in order to find new products that comply with specific application requirements. Each application has a specific function, but normally all aim:

- the production of lighter structures that allow lower fuel consumption

- increased safety and comfort for both crew and passengers

Furthermore, in an era where environmental consciousness is becoming ever more important, the development of greener and more sustainable materials with smaller carbon footprints is catching the attention of the industry. Within the multiple applications in aeronautics industry using sandwich composite materials, aircraft inner fuselage is currently part of the products that have proof the usefulness of such components. In this particular application, the actual challenges for the industry are: weight reduction, increase crew and passengers comfort (thermal and noise insulation) and environmental sustainability.

One of the new materials coming into the spotlight due to its enviable properties, structure and weight is cork. Cork is an excellent candidate for the core of sandwich composite structures, bringing as well the added value of sustainability and low environmental impact.

This dissertation studies the development and implementation of such new composite materials constituted by a cork agglomerate core and carbon fiber reinforced epoxy resin sheets, discussing the main advantages and disadvantages for its industrial implementation. Moreover, this dissertation will present a global overview of the cost breakdown and environmental impact of this specific class of composites.

1

The aircraft industry is constantly looking for new and more efficient components both in terms of environmental performance and of production cost, assuring the safety and comfort of both the passengers and the crew. In this way, the needs of the aeronautical industry in terms on new product development (NPD) rely on its lightness (and consequently less fuel consumption and less costs), comfort providence and environmental sustainability. While the first point is more directed at the direct profit, the other two are specially related to the client's image and overall environmental consciousness.

Taking into consideration these 3 main industry's requirements, composite materials present themselves as both an opportunity and a solution for non structural components in non critical applications. One of these applications is the fuselage layer directly connected to the inner skin that acts as a thermal and noise insulator and that is normally constituted by some type of foam, like illustrated in Figure 1.1. This layer, together with the fuselage inner skin covers the entirety of the fuselage, totaling several hundred square meters which will have impact on the final cost and performance of the aircraft. These fuselage panels must be curved and adaptable to the fuselage shape and must be resistant to the loads in the inner fuselage.

Figure 1.1: Inner skin and insulation layer of an aircraft [1]

Considering these requirements and specific application, this dissertation will consider a new composite material constituted by a cork agglomerate core and carbon fiber reinforced polymer (CFRP) sheets for its insulation properties, high strength to weight ratio, and cork's environmental sustainability.

1.2 Organization

This dissertation is divided into 6 main chapters:

Chapter 1 introduces the theme of the dissertation and its main objectives, providing an overall view of the different topics to be discussed within the thesis.

Chapter 2 presents the composite itself and its structure. It also presents the background for the different materials involved in the production of this new composite, mainly information about their structure, properties, processes and markets.

Chapter 3 presents the different manufacturing processes available for producing composites, the composite design process and the the behaviour one should expect in real cases. It includes the basic

requirements for producing cork sandwich composites and its final application, which should comply with international standards and assure that the final product will fulfill the required needs.

Chapter 4 exposes the environmental impact of the composite and its specific components, paying special attention to the recycling opportunities and technologies.

Chapter 5 analyses the cost breakdown for the production of this composite, taking into consideration the cost of the individual materials, the equipment and the utilities.

Chapter 6 summarizes the main conclusions of this dissertation and indications for further studying.

Appendix A summarizes some of the standardized ASTM tests that composite materials should undergo.

Appendix B performs an analysis of the influences of logistics and supply chains.

Appendix C assesses the reality of the industry itself and particularities of the RD stage, patenting effects.

Chapter 2

Composite Proposal

This study aims at analyzing a sandwich composite with a cork agglomerate core and a carbon fiber reinforced epoxy resin skin like the one in Figure 2.1. This composite has the special purpose of application in the inner skin of the aircraft fuselage. These panels should have special properties like high strength to weight ratios, high resistance under static and dynamic loads, good damping of vibrations, low thermal conductivity and good thermal and acoustic isolation. Sandwich components are also of special interest due to their higher stiffness and better performance under bending which is quite important given the inherent curvature of the fuselage that the panels will be subjected to. The core materials for this sandwich component should have low density, high shear modulus, high shear strength and good thermal and acoustic insulation characteristics [2].
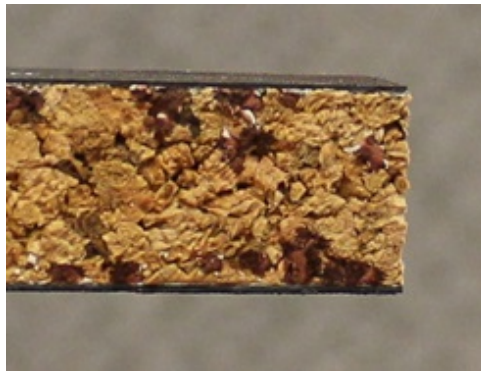
Figure 2.1: Proposed sandwich composite with agglomerated cork core and carbon fiber-epoxy skins [3]

The skins in sandwich structures resist more the bending stresses while the core resists mainly shear stresses. Rigid synthetic foams are often used as core materials and for fuselage insulation however cork agglomerates present themselves as suitable replacements due to its compressive strength, thermal insulation and vibration damping properties. Cork also presents good resistance to fatigue however studies suggest that common cork agglomerates present low static strength which can turn into a problem when dealing with impact loads that would be more critical in structural applications. Comparing cork agglomerate cores with other configurations, it was determined that a cork epoxy agglomerate pre-

sented a core shear stress between 1% and 12% lower that honeycomb cores and 38% to 56% higher than PMI rigid foam cores. Regarding the impact tests, PMI foam cores presented maximum load peak around 2 kN while cork agglomerate cores presented 3 kN [2]. According to [4], after analysis of both NL30 and NL10 cork agglomerates, it was concluded that NL30 had better mechanical properties due to the bigger size of the grains which allowed for smaller particles to fill in the void spaces, increasing density, more joining surfaces and more resistance. However, as noted, lower density is what is intended for a core material and this is why NL10 could also be considered since it has a higher specific shear stiffness. Despite these outstanding properties, it should be noted that the performance of agglomerated cork is far from other typical cores like honeycomb or *Rohacell*.

The skins will be a carbon fiber reinforced epoxy resin sheet which are of particular interest due to its extremely high strength and resistance. To achieve the best possible properties, careful selection of fibers and resins, lay-up geometry and precision and quality control are essential. Carbon fibers have been extensively used in the aerospace industry given the very significant savings in weight: for instance, when the Airbus A320 started the use of carbon fiber composites over aluminium alloys in the horizontal stabilizer, it allowed for a weight saving of around 800 kg and 1 kg of weight reduction allows for saves over 2900 liters of fuel a year. As well, most agile aircrafts have around 40% of their structural mass in composites which cover around 70% of the surface area and the trend is to increase this percentages over the years in both civil and military aircraft as seen in Figure 2.2.
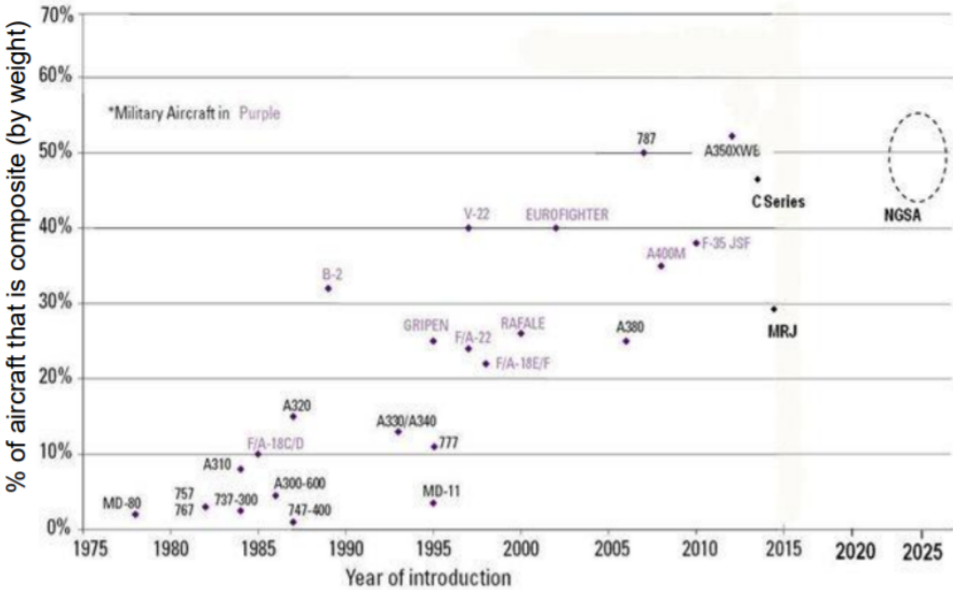
Figure 2.2: Aircraft Composite Content in percentage of structural weight [5]

The use of this composite in the aeronautical industry can be analyzed through the SWOT analysis in Figure 2.3.

For the application in the inner fuselage, given that it is not a structural component and the focus is cost reduction, mainly through weight reduction, NL10 should be the type of cork chosen for the core given its lower density and therefore, better contribution to weight reduction. The CFRP sheets should be produced with epoxy resin and the carbon fibers used should have lower electrical and thermal

Figure 2.3: SWOT analysis for the proposed composite material

conductivity and higher Young's modulus to assure more stability of the fuselage inner skin.

The proposed sandwich composite will contribute both to the overall comfort of passengers and crew by being a source of thermal and acoustic insulation, and to the fuel and cost efficiency of the aircraft for its low density and high specific strength.

2.1 Carbon fibers

Carbon fiber is mainly constituted by carbon atoms and it normally presents between 0.005 to 0.010 mm in diameter. It contains at least 92% in weight of carbon. When it contains 99% in weight of carbon, it is considered graphite fiber. It is particularly praised for its endurance, strength, low weight, thermal and chemical stability, creep resistance, thermal and electrical conductivity and it has become one of the most sought after materials in engineering.

Carbon fibers can be produced from different precursors: polyacrylonitrile (PAN), pitch or rayon, however, PAN carbon fibers clearly dominate the market nowadays. The properties of the carbon fiber are highly dependant on the process, weave, angle of the weave, among others, depending as well on the precursors. Regarding the overall consumer market, in 2010, it was estimated a consumption of 34.200 tons of carbon fiber, 9.800 of which for the aerospace industry [6].

2.1.1 Structure

Carbon fibers present a microscopical structure similar to the one of graphite where several layers or sheets of carbon atoms, oriented as the long axis of the fiber, top each other in a regular hexagonal
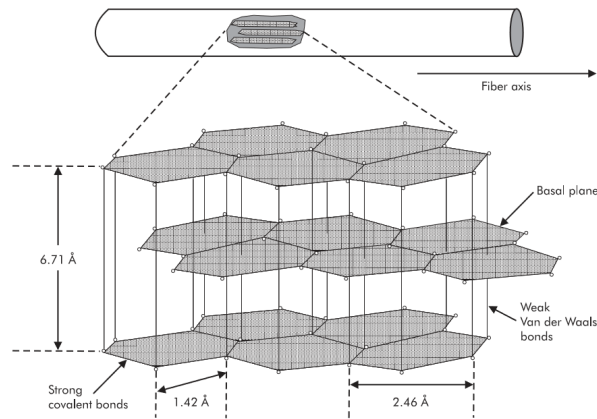
Figure 2.4: Representation of the carbon fiber structure [7]

pattern as seen in Figure 2.4. The covalent bonds within the hexagonal rings are quite strong, adding to the overall strength of the fiber. In the direction perpendicular to the fiber long axis, there are relatively weak Van der Waal bonds that hold the sheets together. Given the weakness of these bonds, carbon fiber sheets tend to present some tendency for surface abrasion which can be reduced by surface treatments [7].

High modulus pitch-based carbon fibers are the ones that present higher orientation compared to PAN-based. All carbon fibers have impurities in its structure, as well as defects, vacancies and grain boundaries. To achieve the best properties in terms of conductivity (electrical and thermal) and tensile modulus, it is essential to achieve low spacing between sheets, higher degree of orientation in the direction of the long fiber axis, low density of defects and high degree of crystallinity [8].

2.1.2 Properties

Carbon fibers present a series of specific characteristics and properties which are responsible for the attractiveness of this material to so many industries. Among them are: [9]

1. High specific strength (force per unit area at failure divided by density)

2. High stiffness, translated in a high Young's modulus

3. Corrosion Resistance and Chemical Stability

4. Electrical Conductivity

5. Fatigue Resistance

6. High Tensile Strength, which means that carbon fibers can withstand high stresses when being pulled apart before breaking. According to [10], the stress-strain curve for single carbon fibers on Figure 2.5 shows this high tensile strengh

7. Fire Resistance

8. High Thermal Conductivity and Low Thermal Expansion Coefficient

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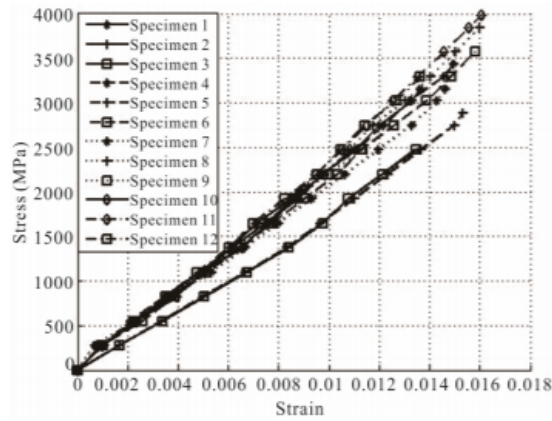
Figure 2.5: Stress-strain curves for carbon fiber specimens [10]

On Table 2.1, general properties of these carbon fibers are listed according to whether they are produced from PAN or pitch: [11]

Table 2.1: General properties for PAN and pitch carbon fibers

Properties	PAN Carbon fibers	Pitch Carbon fibers
Specific density	1.7 - 2	2 - 2.2
Young's modulus (GPa)	200 - 600	400 - 960
Strength (GPa)	1.7 - 5	2.2 - 3.3
Strain at break (%)	0.3 - 2.4	0.27 - 0.6
Thermal conductivity $[Wm^{-1}K-1]$	8 - 105	1000
Electrical conductivity $[Sm^{-1}]$	$6.5*10^6 - 1.4*10^7$	$2*10^6 - 8.5*10^6$

The layers of carbon normally are oriented in the same direction as the long axis of the fiber. This results in a higher Young's modulus in the direction of this long axis compared to the perpendicular direction. Besides the classification of carbon fibers according to the precursor, there is also a different classification according to the properties of these same fibers: ultra high modulus (UHM); high modulus (HM); intermediate modulus (IM); low modulus and highly tensile; super high tensile. The ranges of tensile properties for these different kinds of fibers are presented in Table 2.2, according to [11]:

Table 2.2: Tensile mechanical properties for different types of carbon fibers

Type of carbon fibers	Tensile Strength (GPa)	Young's modulus (GPa)
High tensile	3.3 - 6.9	200 - 250
IM	4.0 - 5.8	280 - 300
HM	3.8 - 4.5	350 - 600
UHM	2.4 - 3.8	600 - 960

There is a tendency for lower Young's modulus as the strength of the fiber increases. PAN carbon fibers also present higher compressive strength than the pitch fibers. Compressive strength is negatively affected by factors such as higher degree of orientation, higher graphitic order and larger crystals. Fibers with higher compressive strength also present an higher shear modulus [11].

Fatigue resistance in carbon fiber is dependant on the maximum stress, stress ratio (minimum stress divided by the maximum stress) and the mean stress. Figure 2.6 shows the different fatigue behaviours
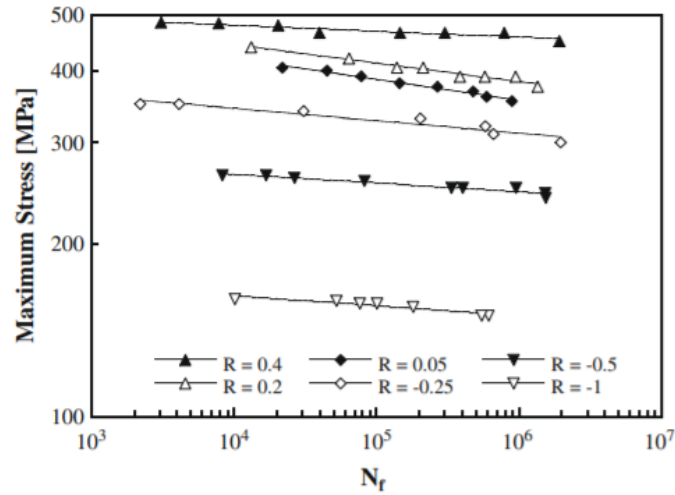
Figure 2.6: S-N curves for different stress ratios in carbon fiber laminates [12]

for different stress ratios. It can be noted that negative stress ratios greatly influence the fatigue strength since there are more failure mechanisms involved and the compressive strength of carbon fiber is lower than its tensile strength [12].

Higher fiber modulus and carbonizing temperature are essential factors for a higher electrical and thermal conductivity while the concentration of defects such as vacancies, interstitial atoms or impurities, contribute to the imperfection of the crystalline structure, reduce these conductivity. Thermal conductivity in carbon fibers is clearly dominated by phonon contributions since the electron contribution represents only around 10% of the total value for thermal conductivity [13].

It has also been showed that corrosion resistance is increased in carbon fibers with higher degrees of graphitisation. The study [14] shows that for a carbon fiber and epoxy composite there were no visual changes in open circuits and up to potential cathodic to -300 mV. White deposits were found at more negative potentials of -650 mV, -900 mV and -1200 mV after 14 days, 5 days and 5 days, respectively. Furthermore, for IM carbon fibers, the coefficient of thermal expansion ranges from $0.4 - 0.8 * 10^6 /°C$ while for HM carbon fibers it rounds $1.6 * 10^6 /°C$ [11].

Besides the presented properties, the longitudinal shear modulus G_{12}, through a torsional pendulum technique [15], was also determined for a PAN carbon fiber. After low temperature carbonizing at 1000 °C, the shear modulus presented a value of approximately 16 GPa and it has been shown that this value does not change considerably with a higher carbonizing temperature [13].

2.1.3 Manufacturing process

A carbon fiber is a fibrous carbon material having a micro graphite crystal structure made from polyacrylonitrile (PAN) precursors, rayon or pitch through a process schematized in Figure 2.7. The PAN process produces fibers with higher strength compared to pitch process and have a higher carbon yield compared to rayon fibers. Although PAN precursors are more expensive, they are the most common type of precursors used to produce carbon fibers. All of these materials are organic polymers, characterized by

long strings of molecules bound together by carbon atoms. The PAN-based carbon fibers manufacturing process typically consists of 6 steps:

1. **Polymerization**

   To form a polyacrylonitrile (PAN) carbon fiber precursor, acrylonitrile (AN) monomers (85 wt% or more) are made to react with other monomers, such as methyl methacrylate, or vinyl acetate, i.e. AN and comonomers are initiated by free-radical reaction and are polymerized either by solution polymerization, bulk polymerization, emulsion polymerization or aqueous dispersion polymerization. These comonomers act like a plasticizer and improve the solubility of the polymer in the spinning solvent.

2. **Spinning**

   Wet spinning is used in most of the commercial manufacturing processes of carbon fibers with PAN precursors, however, it is being replaced by dry jet wet (air gap) spinning. The melt spinning of PAN-based polymer precursors has been a common technique, however, it has yet to become an acceptable manufacturing process of carbon fibers for commercial use. This is an important step because the internal atomic structure of the fiber is formed during this process. The fibers are then washed and stretched to the desired fiber diameter, which helps to align the molecules within the fiber and provide the basis for the formation of the tightly bonded carbon crystals after carbonizing.

3. **Oxidation**

   In order for the fibers to be thermally stable at the atomic level, they should be heated in air to about 200-300 °C for 30-120 minutes, allowing the fibers to pick up oxygen molecules from the air and rearranging their atomic bonding pattern. As chemical reactions occur, heat is generated, which must be controlled to avoid overheating the fibers. The fibers can be drawn through a series of heated chambers or pass over hot rollers and through beds of loose materials held in suspension by a flow of hot air.

4. **Carbonizing**

   Once the fibers are stabilized, they are heated to a temperature of about 1000-1500 °C for several minutes in a furnace filled with a gas mixture that does not contain oxygen (inert atmosphere). Without oxygen, the fiber cannot burn. Instead, the high temperature causes the atoms in the fiber to vibrate violently until most of the non-carbon atoms are expelled. This process is called carbonizing and leaves a fiber composed of long, tightly inter-locked chains of carbon atoms with only a few non-carbon atoms remaining. Graphite fibers could be obtained through a process called graphitization, which is equivalent to carbonizing but at a higher temperature, typically between 1980 °C and 3000 °C. Graphite fibers contain more than 99% elemental carbon, in contrast with carbon fibers, that contain between 93% and 95%.

5. **Surface treatment**

   Usually, carbon fibers need to bond with matrices used in composite materials. For this purpose, after carbonizing, the fibers need to be exposed to an atmosphere that contains oxygen, which in turn oxidizes the fiber surface, improving its chemical and mechanical bonding properties. This can be achieved by immersing the fibers in various gases such as air, carbon dioxide, or ozone; or in various liquids such as sodium hypochlorite or nitric acid. The fibers can also be coated electrolytically by making the fibers the positive terminal in a bath filled with various electrically conductive materials. The surface treatment process must be carefully controlled to avoid forming tiny surface defects, such as pits, which could cause fiber failure. These flaws can have a considerable impact on the fiber tensile strength, but little effect, if any, on modulus, conductivity or thermal expansion.

6. **Sizing**

   To protect the fibers from damage during winding or weaving, they are coated with materials like epoxy, polyester, nylon, urethane, and others, depending on the polymeric matrix that the fibers will reinforce. The coated fibers are then wounded onto cylinders called bobbins. In many companies, the PAN precursor composition and the treatment method of the surface of carbon fibers is kept confidential.

As mentioned, carbon fibers can also be produced from pitch. Pitch is a viscoelastic material composed of hydrocarbons and it is produced from some raw materials like plants, crude oil or coal. The process for the production of the pitch-based carbon fibers is very similar to the one followed for the PAN-based carbon fibers. The most important point for these type of fibers is the mesophase pitch, which means that the fibers are formed from a gelatinous pitch, a state between solid and liquid. This mesophase pitch forms a thermotropic crystal, which allows for the pitch to form linear chains without the application of any tension. Pitch-based carbon fibers do not require the constant application of tensions during the production stages, unlike PAN-based fibers, and have a more sheet-like crystalline structure while PAN-based fibers have a more granular structure [6].
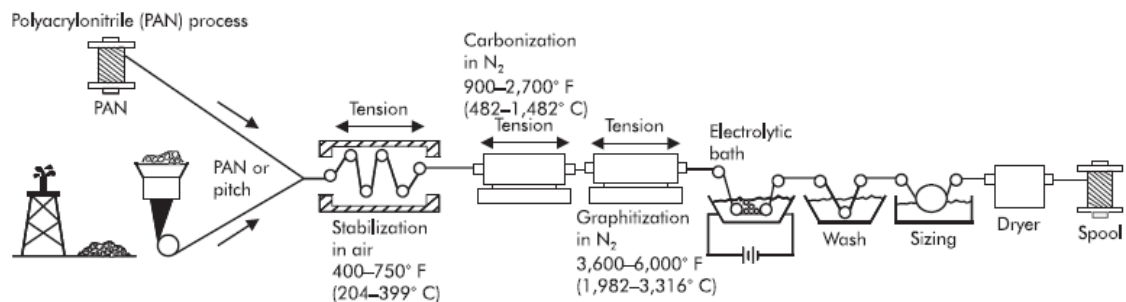
Figure 2.7: Diagram representation of PAN-based and pitch-based carbon fibers production [7]

2.1.4 Market

The annual demand for carbon fibers globally fixed in 63.5 thousand tons, with Western Europe and North America dominating the demand with approximately 60%, while the Pacific and China region hold 23% of the share, and Japan holds 12% alone. Regarding production capacity, a total of 136.5 thousand tons was estimated with 36% of this capacity located in the USA and Mexico and 20% located in Japan. This larger share is explained by the amount of factories located in these territories, specially with the new investments of MCCFC in Japan and of Toho Tenax and DowAksa in the USA [16].

Normally, carbon fibers are fused in a matrix material in order to obtain better properties and these can fall under the following categories: Metal Matrix Composites (MMC); Ceramic Matrix Composites (CMC); Carbon Fiber Reinforced Carbon (CFC); and Carbon Fiber Reinforced Polymer (CFRP) which forms the vast majority of the global carbon composites market as they constitute 70% of the total turnover (19.31 billion US dollars) and 86.5% of the total volumetric amount (126.7 thousand tons). CFRP represent one of the most important investments in the future for the industry as it is the lightweight design material of excellence.

Figure 2.8 shows the global demand for both carbon fibers and CFRP and it can be noted that both graphs are quite similar since a big part of the carbon fiber demand is canalized to the production of CFRP. Profitability for carbon fiber has remained constant for the past years mainly because the market is very concentrated and dominated by a reduced number of companies; when it comes to CFRP, the situation is different since there are more players involved which results in more competition and lower profit margins despite contributing for the faster and more efficient development of the market itself [16].
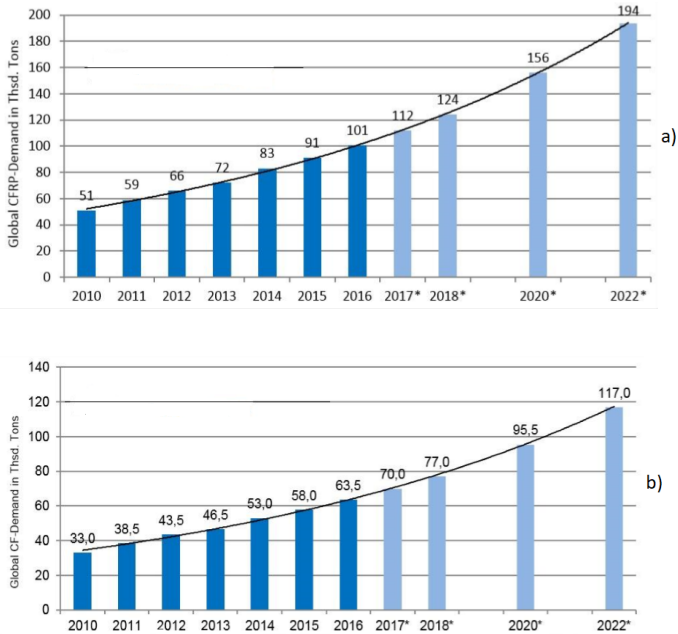
Figure 2.8: (a): CFRP Global Demand; (b): Carbon Fiber Global Demand [16]

2.2 Resins

To produce a CFRP, it is necessary to use a polymer matrix, in this case, a resin which will greatly enhance the properties of the carbon fibers. There are 3 main types of resins: polyester, vinyl ester and epoxy.

Unsaturated polyester resins (or thermoset polyesters) the most common thermoset resin in the composite industry and they are particularly used in the marine industry and normally consist of a solution of polyester in styrene, being this last component responsible for reducing the viscosity of the resin and link the molecular chains of polyester (cross-linking reactions). This type of resins is called contact or low pressure resins since it can be moulded without the application of pressure. They cannot be stored for a long time, otherwise they will gel and not be suitable for use anymore. Polyester resins are considerably cheap and work well with fiberglass however they have poor bonding capability, poor durability, brittleness and should not be used with carbon fiber or aramid [7]. The chemical structure of thermoset polyesters is shown in Figure 2.9.
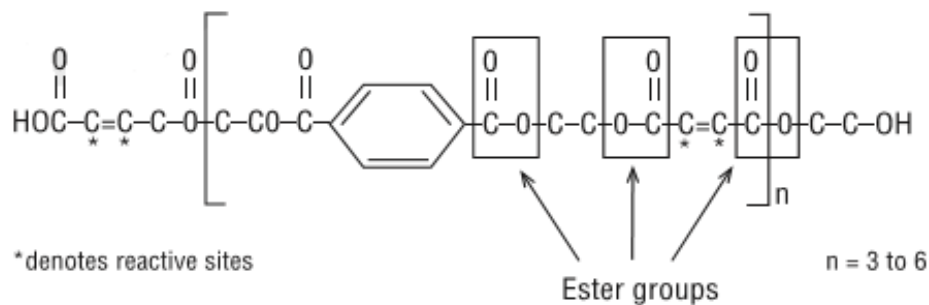
Figure 2.9: Chemical structure of a isophthalic polyester [17]

Epoxy resins come in second place when talking about usage in the industry, after thermoset polyesters, and they are the ones with the best performance indexes given their better mechanical properties, strength, low conductivity, thermal stability and resistance to degradation and environmental attacks. For these reasons, it is the preferred resin type in aerospace applications and it will be the one used in this analysis. Epoxy resins are widely used as coating or painting in ships, metal pipes, cars and industrial machines. The chemical structure of epoxy in Figure 2.10 shows the reactive sites at both ends of the chains (epoxy groups) and two rings in the center which allow for better thermal and mechanical stress absorption than linear chains. These resins have low viscosity, are easier to cure at low temperatures from 5ºC to 15ºC depending on the curing agent, present a low shrinkage during cure, have high strength and chemical resistance. Instead of using a catalyst during the process of curing a epoxy resin, a hardener (curing agent) is used whose molecules react in addition to the resin molecules with a fixed ratio. For this reason, it is very important to use a correct mix ratio so that the reaction takes place until completion. Of all the 3 types of resins presented, epoxies are the hardest to cure [17].

Vinyl ester resins are the least used in the composite market and they present some unique properties like the combination of chemical resistance with affordable price. They present a similar structure to polyester but have reactive sites at the end of the chain which makes this resin tougher than polyester
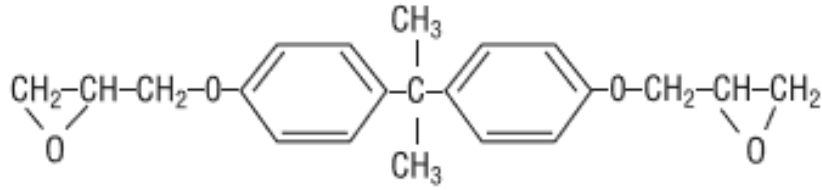
Figure 2.10: Chemical structure of a typical Epoxy [17]

since the whole chain is able to absorb impact. It also has better water resistance than polyester and that is why it is often used as a coat protection for a polyester laminate that will be exposed to water. Regardless, it tends to adhere poorly to carbon fibers or aramid. The chemical structure of vinyl esters is shown in Figure 2.11.
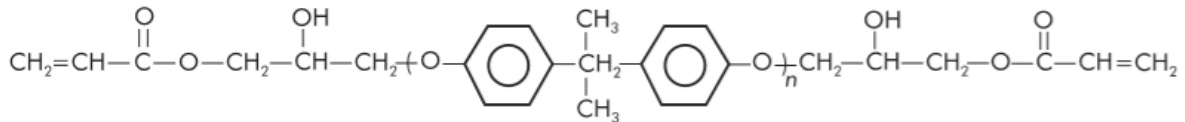
Figure 2.11: Chemical structure of a Bisphenol-A vinyl ester [7]

As referred, epoxy resins present the best mechanical properties regardless of the curing time as seen in Figure 2.12. Polyesters and vinyl esters present considerable molecular rearrangement and shrinkage during curing, something that happens much less extensively with epoxy resins. They also have the best adhesive properties whether it is to the fiber reinforcement or to the core material.

When subjected to water immersion, all resins will absorb water, leading to degradation, added weight and loss of mechanical properties. According to [17], after water immersion for 1 year, a polyester laminate will retain 65% of its interlaminar shear strength while an epoxy laminate will retain 90%.
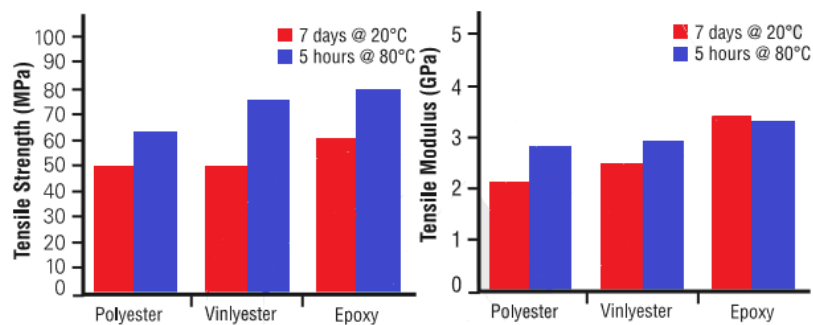
Figure 2.12: Comparison of tensile strength and modulus of different resins [17]

2.3 Cork

Cork is the bark of the oak *Quercus suber L.* harvested typically every 9 to 12 years depending on the region. Each tree needs 25 years before it can be harvested for the first time and they have a life span

between 250 and 300 years. This botanic species is characteristic of a Western Mediterranean climate with its most important regions being Portugal, Spain, Southern France, part of Italy and North Africa. This bark plays a function of protection of the oak tree, insulating it from heat and from loss of moisture. It is a vegetal tissue composed by an agglomeration of cells filled with a gas mixture and lined with layers of cellulose and suberin intercalated.

After being harvested, the cork should be put in rest for 6 months in order to stabilize after which it is boiled in steel closed and filtered tanks in order to meet the criteria for industrial use. Through this process, the organic impurities present in the pores are removed and the material can reach the ideal moisture content for the upcoming processing.

It has been considered one of the most versatile materials for centuries and, recently, it has been greatly associated to sustainable development policies when it comes to maintenance of biodiversity and reduction of CO_2 emissions. Lead environmentalists have been advocating for the use of cork due to its capability to save energy, to reduce greenhouse gas emissions, to its recyclability and to the fact that the cork is a material harvested from living trees that renovate on their own. In a world where environmentally conscious practices are each time more important, cork is gathering special attention from engineers, architects, technicians and even by consumers themselves.

The fact that the cork is harvested periodically allows for an even greater fixation of CO_2 since the oak tree produces between 250% and 400% than it would produce if it was not exploited. In this way, it is estimated that the cork oak forests allow for the sequestration of until 5.7 ton CO_2/ha/year. Being that there are around 2.3 million acres of oak forests worldwide, the retention is estimated at 14.4 million tonnes CO_2/year. Besides this, cork is carbon neutral, which means that, when incinerated, the CO_2 emitted equals the amount that was stored in the material itself [18].

2.3.1 Microscopic structure

The structure of cork has already been studied for some time, for the first time by Robert Hooke in the XVII century who examined a thin section of cork under the microscope. The more detailed microscopical structure of cork was only revealed after analysis under scanning electron microscopy (SEM) in 1987.

Cork presents a structure similar to the honeycomb one where adjacent regularly arranged cells, also known as *alveoli* without empty spaces between them follow each other. These cells are limited by thin-walled cells constituted by an homogeneous tissue. When looking at a tangential section, it can be seen that the lateral cell walls do not have a particular direction, suggesting that the material is transversally isotropic, which means that the directions perpendicular to the radial direction should be equivalent. The cell walls are thinner if produced in the spring or summer, ranging from 1 to 1.25 μm and thicker in autumn or winter, ranging from 2 to 2.5 μm [19]. This fact, associated with the larger and smaller cell dimensions, also interferes in the mechanical and physical properties of cork. These cells present a structure of rectangular prisms that follow each other in columns parallel to the radial direction of the oak tree. The prism structure of the cells is variable since the polygons at the base can vary

from 4-sided to 9-sided although heptagonal, hexagonal and pentagonal bases are most common. Its average dimensions are from 30 to 40 μm in width and from 35 to 45 μm in height.

Figure 2.13 depicts the structure described both radially and tangentially:
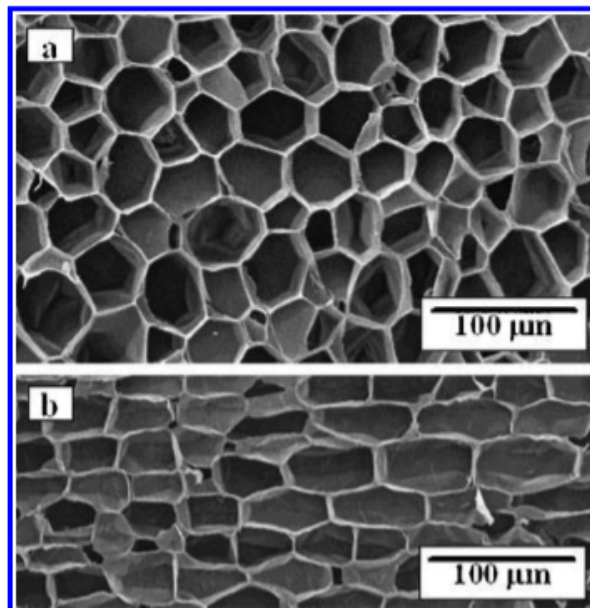
Figure 2.13: SEM visualization of natural cork after boiling: (a) radial section; (b) tangential section [20]

On the lateral faces of the prisms of the cork cells, irregular wrinkles are often observed despite the existence of cells with almost no evidence of this phenomenon. The compression the cells suffer during the growth of the tree is most likely the cause of these wrinkles.

The fact that the cells are filled with a gas mixture mainly composed of air, as well as the fact that the cork cells are extremely small when compared to other materials give to cork its unique insulating properties.

2.3.2   Macroscopic Structure

The harvesting of cork trees, represented in Figure 2.14 is cyclical, taking place usually every 9 to 10 years when the diameter reaches 25 cm. The material harvested at each time presents significantly different structures: virgin cork is very irregular in its thickness and density, besides not being consistent and firm. As successive harvests take place, the material becomes more regular and with a smoother texture. Second reproduction cork already presents a quality considered high enough for the production of wine stoppers since this industry demands high standards when it comes to the visual defects and colour consistency of the material.

The extraction of cork exposes the exterior part of the inner bark that starts being pushed outwards by the formation of new cells that are the cork itself. In this way, the cork is formed between the inner bark and the outer bark which, in its turn, presents a diversity of breaches and cracks due to the growth of the cork beneath it. This tissue grows from the inside to the outside which means that the most recent layers, with less elasticity and more porosity, are the ones closer to the inner bark of the oak tree. In

Figure 2.14: Cork harvesting in Portugal

Figure 2.15, the different stages of this growth can be observed.

Analysing the radial rings of the cork, it can be noticed that they are different in size and thickness which is indicative on whether that period of growth happened in the spring/summer or in autumn /winter. Before all further processing, cork goes through a boiling phase aimed at making the cork more pliable and uniform given that the heat will cause the gas inside the cells to expand, removing the wrinkles from the walls and tightening the cork.
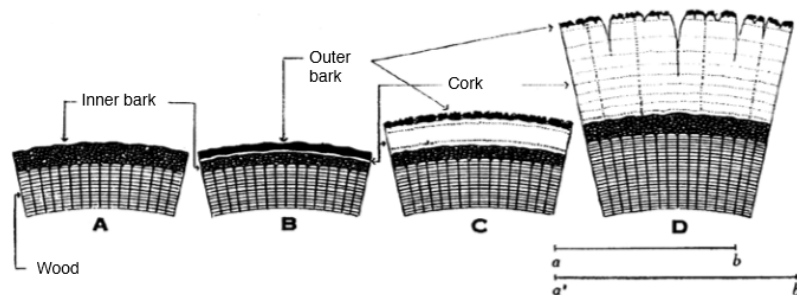
Figure 2.15: Different stages of the cork growth in the oak tree [19]

2.3.3   Chemical composition

The chemical composition of cork is not the same for every piece since it is widely dependant on the soil, climate, geographical origin, size of the tree, age, among others. Typically, this composition is presented as follows:

- Suberin, ~45%, explains the cork's compressibility and elasticity

- Lignin, ~27%, compound of the cell walls

- Polysaccharides, ~12%, linked with the structure of cork

- Wax, ~6%, responsible for the impermeability of cork

- Tannins, ~6%, responsible for the conservation and protection of the material

- Ash, ~4%

2.3.4 Properties

One of the most essential studies when analyzing the mechanical properties of a material is the stress-strain curve depicted in Figure 2.16. This stress-strain curve is characteristic of every material and it records the level of deformation for different loadings applied. Analyzing this curve, it can be noted that there are 3 different phases typical of flexible cellular material: firstly, until around 7% strain, the cell walls bend in the purely elastic domain; secondly the curve reaches a more horizontal level where the cell walls buckle leading to progressive instability; finally, starting from around 70% strain, the cell walls collapse and the curve rises exponentially.
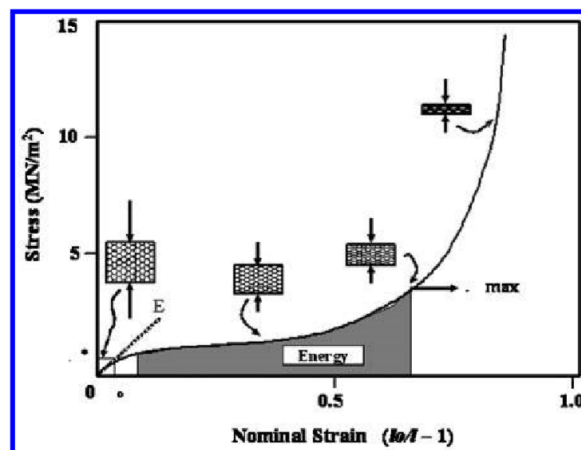
Figure 2.16: Compressive cork's stress-strain curve [20]

Another interesting mechanical property of cork is its Poison's coefficient, ν, which is the ratio between transverse contraction strain and longitudinal extension strain in the direction of the applied force. Most materials present a positive value for the Poison's coefficient since when a sample is stretched in one direction, normally shrinking can be observed in the other two directions. Given that the microscopical cell bases are fairly randomly arranged, when cork is compressed in the radial direction, the cell walls are compressed, folding on each other like an accordion, thus increasing the amplitude of the wrinkles already naturally present, and the cell bases align which causes a small expansion in the axial and tangential direction. In this way, for radial compression, cork presents a small positive ν. When compression is applied in non-radial directions, bending forces act on the cells' lateral walls, straightening them and leading to a small expansion in the radial direction. However, if compression is taken to higher values, the wrinkles are inversed, leading to a a contraction in the radial direction and thus, to a negative Poisson's coefficient [21]. The mechanism for both radial and non-radial compression is pictured in Figure 2.17.

Cork does not grow uniformly which leads to different thicknesses along the cork planks; this thickness is called the calibre and has an important influence on mechanical properties. In compression, planks with higher calibre tend to have lower strength and Young's modulus which can be mainly explained by the higher degree of dissimilarity in cell dimension and undulation patterns.

As mentioned, cork goes through the industrial process of boiling, a water heat treatment, that affects
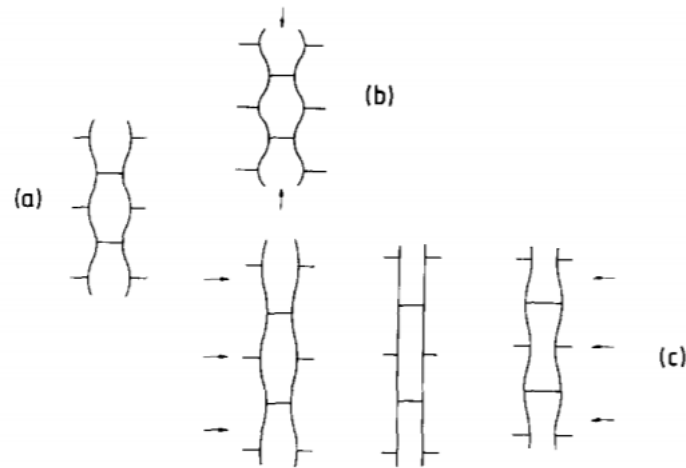
Figure 2.17: (a) and (b): increase of wrinkles' amplitude due to radial compression; (c): inversion of the undulations due to non-radial compression [21]

directly the mechanical properties of the material. Water is absorbed by the cork, softening its walls and straightening them by action of pressure differences between cells. This leads to a reduced strength, reduction of anisotropy, as well as a more abrupt yield point for compression in the radial direction. Some general mechanical properties of cork can be found in Table 2.3 , according to [20].

Table 2.3: General properties of cork: R for radial direction, NR for non-radial direction

Property	Value
Compressive modulus of boiled cork $[MPa]$	6 (R) ; 8-9 (NR)
Tensile modulus of boiled cork $[MPa]$	38 (R) ; 24-26 (NR)
Fracture stress under tension $[MPa]$	1.0 (R) ; 1.1 (NR)
Fracture toughness of boiled cork $[MPa\,m^{1/2}]$	60 - 130
Poisson's ratio of boiled cork	0-0.97 (R/NR) ; 0-0.064 (NR/R) ; 0.26-0.5 (NR/NR)
Friction coefficient boiled cork/glass and boiled cork/steel	$0.2 - 1.2$
Density virgin cork $[kg/m^3]$	$160 - 240$
Thermal conductivity $[Wm^{-1}K^{-1}]$	0.045
Electrical conductivity at 25 Celsius degrees $[Sm^{-1}]$	$1.2*10^{-10}$
Specific heat $[Jkg^{-1}K^{-1}]$	350
Thermal diffusivity $[m^2s^{-1}]$	$1*10^{-6}$

The density of cork is widely variable depending on factors such as age and treatment of the material, with variations between 120 to 240 kg/m^3. A higher level of undulations in the cell walls corresponds to a higher density of the material. The process of cork boiling also leads to a decrease in density since thus heat treatment reduces the wrinkles of the walls, expanding the material in terms of volume. The low density and high porosity of cork are usually some of the most sought for characteristics of this material and it is mainly due to the high gas content in the interior of the cells. This means that thermal conductivity and sound transmission are rather poor: since transmission of heat in cork is by conduction, which is highly dependant on the amount of solid in the material, most is lost through the maze of cell walls and gas; sound waves are mostly absorbed by cork and transformed in heat, reducing sound reverberation.

2.3.5 Market and Applications

In order to analyze the cork market, it is specially interesting to look at the Iberian market since it represents more than 80% of the global production and around 60% of the total cork oak forest worldwide, according to a 2012 study by APCOR (Portuguese Cork Association). Nowadays, Portugal is global leader in cork industry and in manufacturing cork; Spain remains focused in the unmanufactured cork industry, most of which is exported to Portugal for further processing.

According to the study [22], in 2012, the Iberian Peninsula produced 161.504 tonnes of cork, 49.6% by Portugal and 30.5% by Spain. This industry as quite an important economical impact in each country, representing 1.5% and 1.2% of the Portuguese and Spanish industrial output, respectively. This economical impact also translates to employability, with almost 12.000 workers in around 800 companies in the region. The Iberian Peninsula imports 23.553,16 tonnes (49 million US Dollars) and exports 174.050 tonnes (1147,5 million US Dollars). It is clear the considerable gap between imports and exports and the monetary income that the industry represents for both countries. The most imported products are raw material and natural cork stoppers while the most exported are agglomerated cork and natural cork stoppers. Over 60% of the imports come from Northern Africa, mainly of raw material while the remaining imports come from other European countries mainly. Exports are mainly directed at Germany, France, Italy, Russia and the USA.

Portugal imports raw cork to process it, transforming it in other final products aimed at exportation; in this way, the monetary value of this natural resource is increased since the raw cork is imported at low prices. On the other hand, Spain focuses mainly on the production of raw cork and some manufactured cork products. Figure 2.18 shows some of the diverse applications of cork nowadays:

One of the most iconic applications for cork is wine stoppers and it used to be the main product for this material. Nowadays, as a result of significant investment in innovation and product development, cork is being targeted for the transportation industry, construction, architecture, composites, aerospace, among others.

Cork has always been regarded as the ideal material for stoppers due to its interaction with the wine, developing some of the unique qualities of this product. These can be obtained by extraction in one piece from a cork plank or by agglomerate moulding or extrusion from granulated cork. Cork has been getting some special attention from the construction industry, specially when it comes to floor and wall coverings given its thermal and acoustic properties. For this last purpose, expanded insulation cork is particularly interesting: it is produced from *falca*, a kind of cork from the upper branches of the oak, which is pulverized to granules and then heated in an autoclave, expanding and binding with the other granules without the addition of special binding agents. Granulated cork can be produced with different sizes with mass densities ranging from 40 to 100 kg/m^3 also has diverse applications in fields such as electronics, chemistry and engineering.
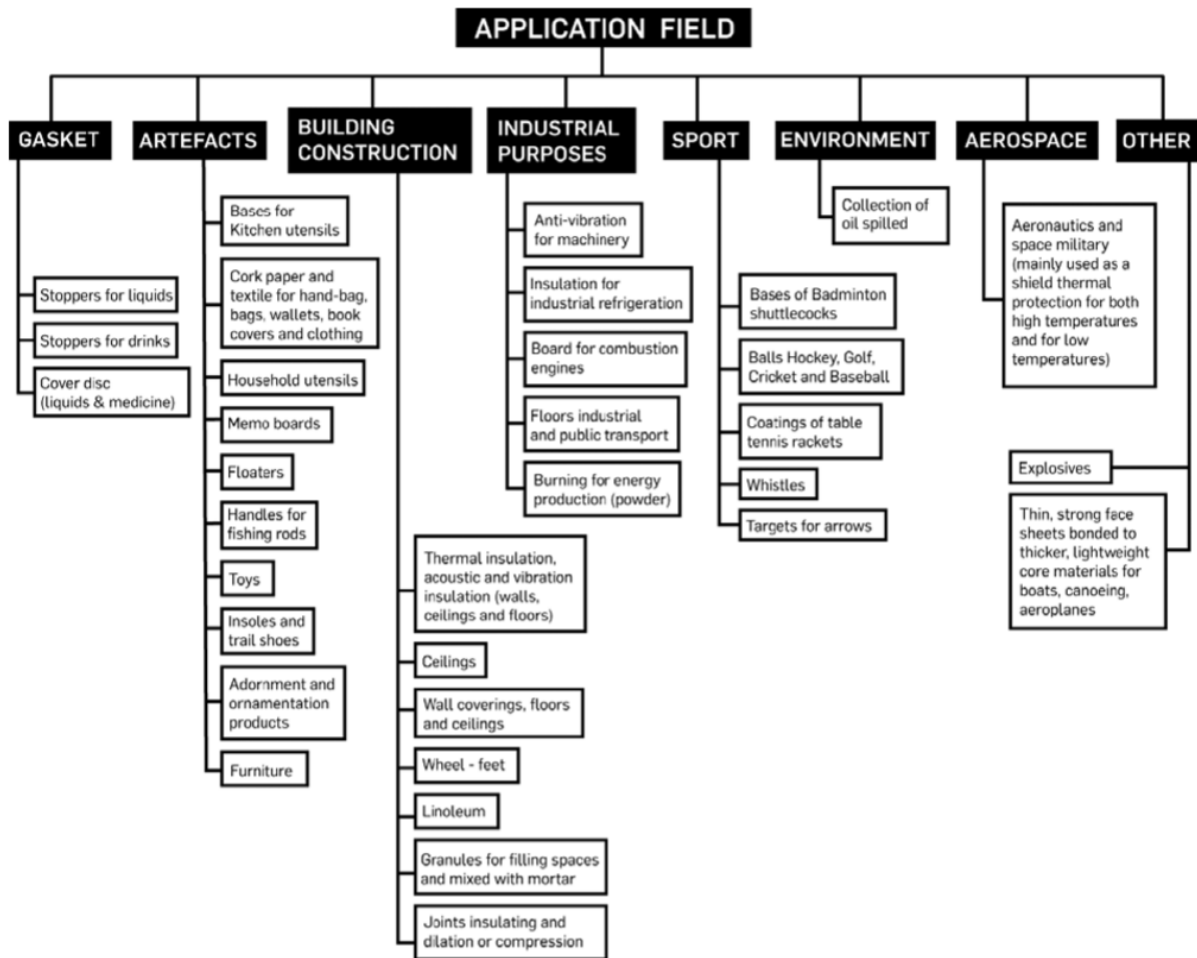
Figure 2.18: Multitude of cork applications [23]

Chapter 3

Composite Production

The proposed composite material must meet the requirements for its specific application and the manufacturing method for it is essential to achieve it since final properties greatly differ based on the method used. This composite material should be designed with the task of meeting the user's need by analyzing the four main elements of materials science: processing, structure, properties and performance. These elements connect between each other in a chain according to Figure 3.1. This chain can be looked at in different ways according to the reasoning behind it, whether it is deductive or inductive. By the deductive cause-effect logic, the achievement of specific properties and performances is analyzed taking into consideration and starting with a series of materials, processes and structures. By the inductive goal-oriented logic, we start from a specific property of the material that is desired and analyze which materials could achieve that [24]. In this specific case, the inductive goal/means logic is more appropriate since the inner skin of the fuselage has specific requirements that have to be met by the candidate material in order to be suitable.
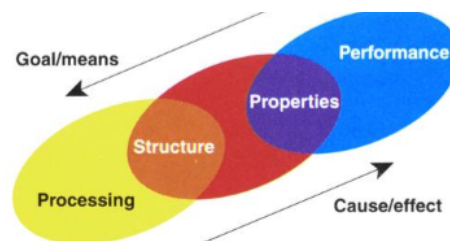
Figure 3.1: Chain between the four main elements of materials science [24]

The panels should be designed, taking into account important factors such as type of loading, mode of loading, service life, operating environment, manufacturing processes available and costs. It is essential to predict the stresses and strains expected for the composite material to withstand, determining design allowables which are limits of stress, strain or stiffness expected at the most severe environmental conditions allowed for a given material. To assure maximum safety, safety factors are applied to these design allowables so that failure does not happen due to certain uncertainties like stress concentrations, calculation errors, fabrication processes and material aging. For aeronautical structures, the typical safety factor is 1.5 which means that any structure that has to withstand a certain limit load, should be

designed to withstand a load equal to 1.5 times that limit. However, for composite materials, the safety factors applied are often of 2 or more given the lack of extensive experimentation and design knowledge with this kind of materials. In the special case of composite materials, lack of knowledge is a problem given the huge range of different composites and the difficulty to have information on behaviour and response to certain factors. As well, there is no design software appropriate for all the design phases. This fact also complicates the development of trade studies where many design and materials are compared in order to choose the most appropriate one [25]. In the fuselage inner skin, the panels will be particularly subjected to radial compressive tensions due to cabin pressurization, shear loads due to loading distribution and compressive axial loads due to bending moments.

3.1 Manufacturing

Regarding the cork for the sandwich core, the cork granules size is one of the most important factors. For instance, Corticeira Amorim provides these with 1mm, 2mm or 3mm as shown in Figure **??**. When only granules with the same size are used, there are more voids left out that are usually filled in with a resin, resulting in a more reduced density. It has been proven that mixing different granule sizes leads to better mechanical properties due to better bonding between the particles [26].

In order to fabricate this particular complete composite, there are a series of manufacturing processes that can be used that are summarized below according to [27]. Note that both the core and the sheets should first be produced separately and only after joined. Since the curvature is the same for both parts, the mold used could be the same since only the thickness would differ.

- Injection Molding: pellets of solid thermoplastic resin are mixed with the particles and placed in a hot barrel with a rotating screw that will melt the resin by friction (viscous dissipation) and also electrical heating of the barrel. This screw also will force the mixture into a metal mold container where it will cool off and solidify as in Figure 3.2. The cycle for each part is quite short and the process is automatic allowing for high volume production however the equipment and mold costs are quite high and it does not allow for control of fiber orientation and distribution. This process is specially suitable when thermoplastic resins are used which is not the case of epoxy. This process would only be suitable for the individual production of either the core or the sheets but not for the assembly of the final sandwich.
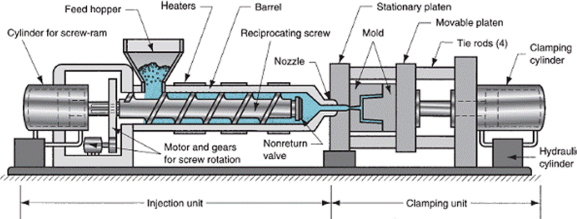
Figure 3.2: Representation of Injection Molding [28]

24

- Resin Transfer Molding: the particles are inserted into a mold tool that has the shape of the desired piece. A second mold is placed on top and resin is injected into the space between the two molds as in Figure 3.3. On one end of the piece, a vacuum pump can be used to help with the flow of resin throughout the mold in what is called Vacuum Assisted Resin Injection (VARI). The purple line in Figure 3.3 represents the fiber preform that is placed in the mould before the resin injection, which is already in the form of the final product. These methods are suited for complex large scale structural parts and it is advised for fast thermosetting resins such as epoxy.
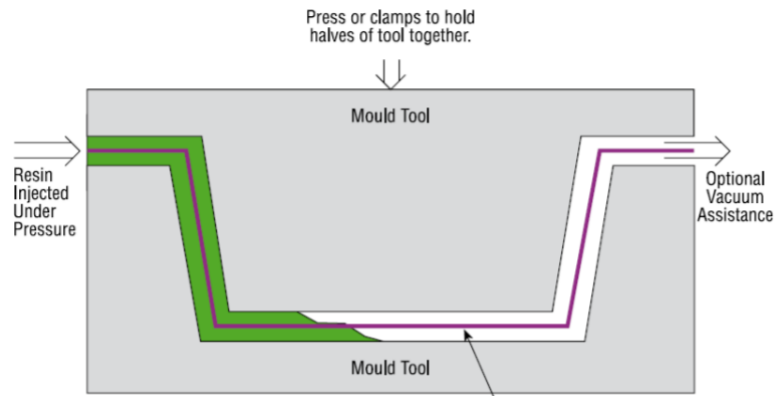
Figure 3.3: Resin Transfer Molding basic representation [29]

- Compression Molding: the mixture of resin and fibers or particles is placed inside the mold cavity to which is then applied a pressure up to 2000 psi leaving the material with the form of the mold as in Figure 3.4. This is a relativelty simple process, fast and with high repeatibility advantages however the molds can be quite expensive and there can be some small defects due to stresses, delamination and warpage.
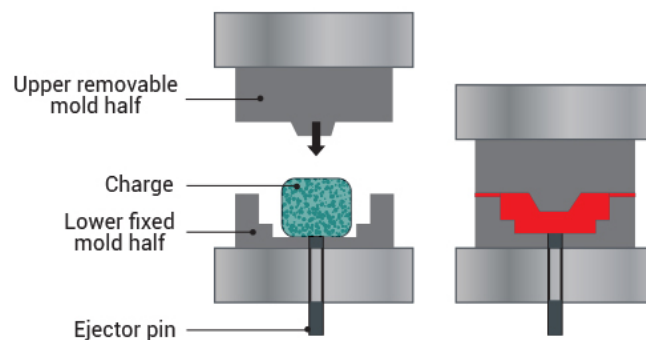
Figure 3.4: Representation of Compression Molding [30]

- Vacuum Bagging: the composite is placed on top of a single-sided mould and covered with a vacuum bag which will be sealed around the part as shown in Figure 3.5. A vacuum pump is then used to remove the air and the part will be consolidated under the atmospheric pressure. This process can be undertaken in an oven for resin curing. This is specially suitable for large parts and does not require high maintenance costs due to the relatively low pressure of 1 bar. The fact that the pressure is not as high as in other processes also limits the performance of the final part.
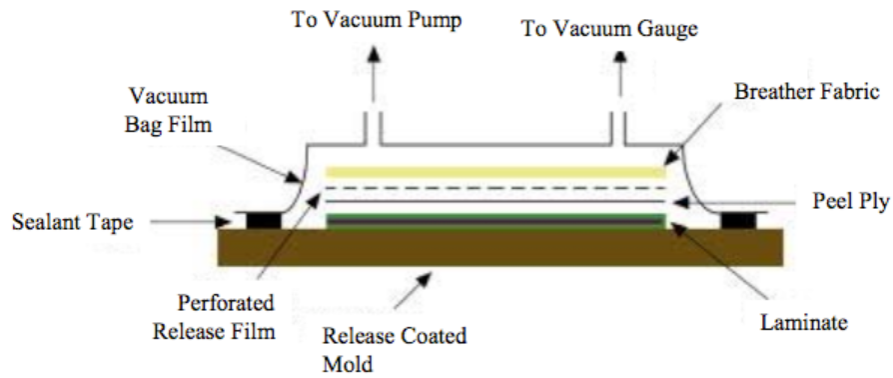
Figure 3.5: Representation of Vacuum Bagging [31]

- Pultrusion: fibers are pulled through a resin bath and then through a small oven where they are cured as in Figure 3.6. This process is suitable for parts with constants cross sections and thermosetting resins and it normally presents rather smooth results. This process would not be suitable for the wanted component since it would compromise the curvature.
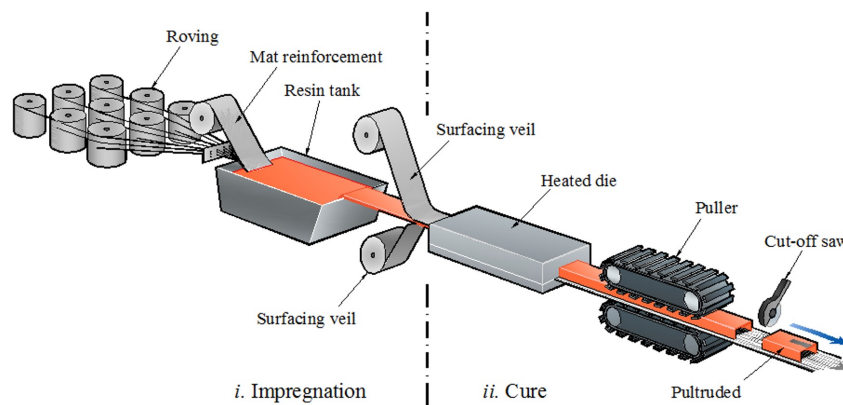
Figure 3.6: Representation of Pultrusion [32]

- Autoclave: there are sophisticiated containers where composites are introduced already in a vacuum bag, so that they are subjected to elevated temperatures and pressures, improving mechanical properties, resin curing and fiber to resin ratios. The pressures applied usually go up to 1.5 MPa. These autoclaves are quite expensive and require a considerable investment however this method is the one that delivers the best product quality and reliability.

For the production of the sandwich composite, there are three main candidates: compression molding, vacuum bagging and autoclave. In a previous stage where mass production is still not needed, and in order to explore the possibilities for this new composite, vacuum bagging, following the standard ASTM D5687, is a good option considering its low cost and medium part strength [26].

Regarding the mass production of this composite, closed forming processes seem to be more suitable and produce better results. Out of these, vacuum bagging presents the lower equipment cost while the autoclave presents the highest. Reproductibility is better in compression molding while lower in vacuum bagging. The autoclave process allowed for the obtention of composites with the highest values

of impact strength and Young's modulus as well as almost total absence of discontinuities. Methods of compression are cheaper than autoclave and produce similar results when it comes to mechanical properties. Vacuum bagging also achieves quite acceptable results and it is much more low cost [33]. There is also a possibility to add other fillers to the cork composite such as micro fiber, silicon dioxide cotton flock or chopped glass strand that will enhance certain mechanical properties such as the internal bonding of constituents (micro fiber) or the introduction of a more complicated microstructure (chopped glass strand). Bonding of the cork core with the CFRP sheets is also extremely important as this will be determinant in the overall impact strength of the composite and it should be done by introducing a layer of resin and hardener between both components. [26].

Considering the shape of the panels and considering that both the core and the sheets have already been produced accordingly, compression molding would present as a suitable manufacturing method since it allows for high reproductibility which is needed given the extent of area that has to be covered. Regarding the final mechanical properties, they would not differ much from the ones achieved with the autoclave (process which would lead to the best mechanical properties), with the added value of being much more cost efficient.

3.2   Design Requirements and Behaviour

Taking into account the final application of this composite in the inner skin of the fuselage, some specific properties are required:

- Low density

- Low electrical conductivity

- Low thermal conductivity

- High strength to weight ratio

- Fire Resistance

- Corrosion Resistance

- Shear Resistance

Sandwich structures are often compared to the I-beams used in civil construction: while the horizontal flange of these beams resist more bending moments, the vertical elements support mainly the shear forces and the same happens with sandwich structures with the core resisting more shear loads and the facings the bending. Therefore, the shear properties of the core material as well as its thickness are extremely important given that just doubling the total thickness of the core results in an improvement of the total stiffness of the composite by a factor of 7 [26].

According to [34], natural materials such as cork as cores in sandwich structures present lower magnitude of noise radiation, measured by wave number amplitudes, compared to traditional synthetic

cores which would be an added value for this core when comparing cork cores with synthetic foams normally used. Furthermore, if these natural core materials have low specific shear modulus, the acoustic performance is improved.

Composites have limited resilience and that presents a problem to aerospace when confronted with impacts and foreign objects damage however, since the desired application regards the inner skin of the fuselage, it would not have to be subjected to considerable impact loads.

In order to test the composite and define the property profile of the same, some tests should be performed as well as computational analysis. In reference [35], drop tower impact tests were carried out with a free falling mass, employing different initial heights, for different impact energies. The impact loads were read with the help of a piezoelectric force transducer placed between the impactor and the load carriage. To assess damage tolerance capability, residual strength characterization after impact based on four-point flexural tests was performed using a servo-hydraullic machine with a 100kN load cell. This kind of test aims at assessing the capacity of a specimen to continue delivering on its functions after an impact which can cause the called invisible damage specially if it is a low velocity low energy impact. Using both a drop weight machine and a static test load, damage tolerance can be estimated using both flexure after impact (FAI) and compression after impact (CAI) tests. Studies on composites show both flexural strength and modulus are reduced as the impact energy increases [36].

The experiments led in [35] resulted in the graphs presented in Figure 3.7 and Figure 3.8.
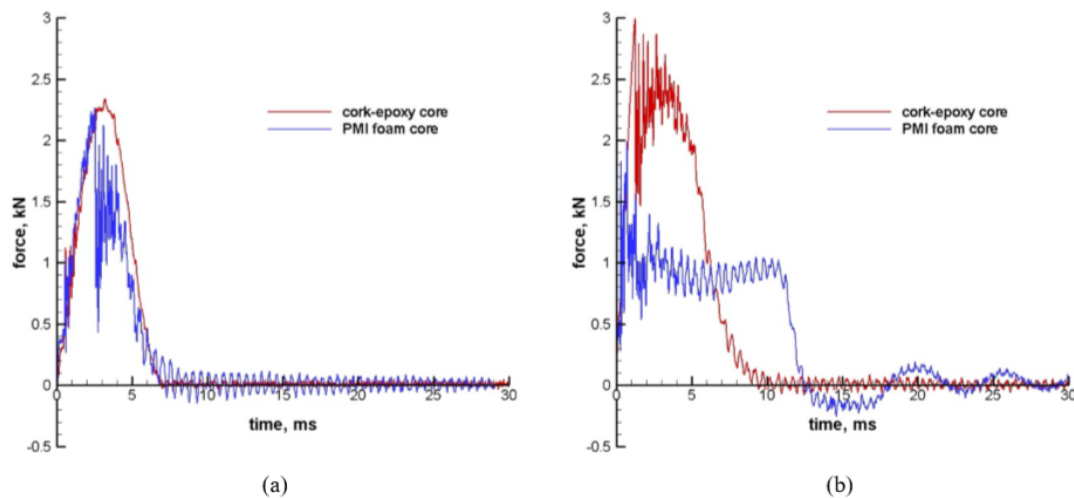
Figure 3.7: Force-time curves for cork-epoxy or PMI foam 30 mm cores for impact energy of (a) 5 J or (b) 20 J [35]

From observation of the force-time curves, it can be concluded that cork cores allow for a smoother response to impact from the less evident oscillations after impact which supports the idea that cork composites allow for higher energy absorption. However, the PMI foam cores show a quicker reduction in the curve after maximum peak is reached as well as a much longer plateau. The force-displacement curve shows that the displacement of the impactor is smaller for the cork-epoxy cores and a rebound was observed. The fact that there is no rebound for the PMI foam core proves that the total energy absorbed is higher causing bigger damage. The shorter time of contact for the cork core also indicates
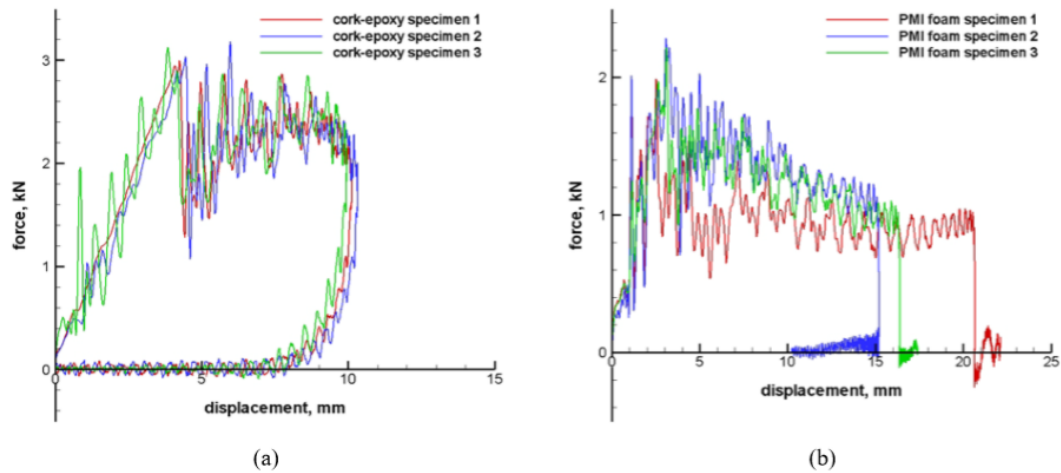
Figure 3.8: Force-displacement curves for (a) cork-epoxy specimens or (b) PMI foam cores for impact energy of 20 J [35]

that there is a higher percentage of elastic energy involved in the form of vibrations and that deformation is more elastical than in the foam core case. Regarding the flexure after impact tests, the study showed that residual flexural strength for non impacted cork core sandwiches were surprisingly lower than the values for impacted specimens with a variation in load limit of +8.9% after the 5 J impact and a variation of +14.2% after the 20 J impact. These results were much better in comparison with the PMI foam core that showed a reduction in bending load limit of -29.7% after the 5 J impact and a variation of -18.8% after the 20 J impact. It was also noted that the damaged area of the sandwich composite was significantly smaller for the cork agglomerate core in comparison with the PMI foam which further testifies for the important energy absorption capacity of this composite in comparison with traditional foams in the same application.

Regarding the CFRP sheets, it is extremely important to assure the alignment of the fibers so that there is no creation of voids parallel to the fiber axis that would act as stress concentrators and weakening the overall skin. The fibers must also be strongly bonded to the epoxy resin matrix as a weak interface between both components will lead to lower stiffness, lower strength, lower resistance to fracture, lower creep resistance and quicker environmental degradation. This bonding conditions should be assured by the carbon fibers supplier as previous chemical etching and sizing are essential to assure a proper resin-fibers interface despite the considerable complexity of this connection. This bond will have special influence in crack growth and propagation since, if it is strong, the crack may propagate through fibers and resin without deviating however, if it is weak, the path followed by the crack it is extremely complex and unpredictable [37].

Unfortunately, research and data about the mechanisms of fracture in composites is still on its early stages which further complicates the design phase of the composites and the achievement of optimal combinations of strength and toughness. Normally, fracture in composite materials does not occur catastrophically as it is progressive and presents damage throughout the composite. The fact that the different mechanisms in composite materials can be quite complex will inevitably lengthen the design process however this is widely compensated by the improvement in aerodynamic behaviour and mass

savings [37].

3.3   Testing and Certification

In order to develop a new material, it is necessary to have a system of testing and norms or regulations to follow in place so that the final product can meet the minimum and specific requirements expected. In the specific case of composites, it can be quite difficult to find a set of standards to follow given the issues such as the complexity of composites, its novelty in the industry, its constant and quick development and the lack of standard tests to apply. Given the ever changing nature of the matrix or reinforcement, composites have to be treated in a completely different manner than metals or ceramics when it comes to its product and process control. The database of composites is fairly fragmented between firms which makes it more difficult to come up with standard tests that can be applied to a wide range of composite materials. In an attempt to create these, some professional societies have been developing norms such as American Society for Testing and Materials (ASTM); Suppliers of Advanced Composite Materials Association (SACMA); National Aeronautics and Space Administration (NASA); American National Standards Institute (ANSI); British Standards Institute (BSI) or International Organization for Standardization (ISO) [7]. ASTM standards regarding the standard testing that composite sandwich structures have to undergo are presented in Appendix A.

Given the value chain for this sandwich composite, all the design and procurement developed has the ultimate goal of certification so that mass production can be initiated. In a regulated sector such as the aeronautical one, production is not possible without certification and that is why this compliance verification phase is of maximum importance.

For the specific case of aeronautical applications, given the extensive regulated nature of it, the proposed sandwich composite would have to comply with a series of regulations in place like the Joint Aviation Requirements in the European case, specified below for this specific application:

- JAR 26.150 (a): Compartment interiors flammability [38]

- JAR 26.155: Flammability of cargo compartment liners [38]

- JAR 25, Appendix F - Part I: Flammability of interior ceiling and wall panels [39]

- JAR 25, Appendix F - Part I: Thermal and acoustical insulation - Insulation covering [39]

- JAR 25, Appendix F - Part I: Insulation on electrical wire and electrical cable installed in any area of the fuselage [39]

- JAR 25, Appendix F - Part Iv: Heat Release and Heat Release Rate for wall and ceiling panels [39]

Given the specific requirements and applications of this sandwich composite on the inner walls of the fuselage, compliance with the JAR regulations above is mandatory for certification and successive production.

Regarding the overall production of the composite, it can be concluded that, after proper production of each component with adequate curvature, the panel can be assembled through compression molding through a fairly simple process. The logistics for the material supply chain would have to be arranged for adequate production, as explained generically for the industry in Appendix B. Despite seeming that this composite would comply with the specific requirements according to research, it could benefit from further innovation, research and development. The theory related to innovation in industry as well as the specifications for RD and patenting can be found in Appendix C.

Chapter 4

Environmental Analysis

The increased usage of composite materials in the industry, coupled with the environmental policies that aim to reduce pollution and change the ecological behavior of both consumer and producer, turns environmental analysis indispensable when addressing the possibility to introduce a new composite in the market. One of the challenges proposed by the manufacturing of CFRP is the lack of industrial scale composite recycling. Industry is still incapable of addressing the waste management for the increasing waste accumulation, which has a global scale impact. Thus, recycling technologies aim to be technologically capable while environmentally beneficial. CFRP recycling is quite difficult due to the problem related to melting thermoset resins and because it often involves harsh chemicals that can damage the fibers themselves and add to the environmental impact due to the hazardous nature of the caustic chemicals [40]. The present chapter firstly addresses the environmental impact of the different components of the composite material and then proceeds to analyse their recycling processes.

4.1   Impact

This composite presents 3 main components that will have a seriously diverse impact on the environment among them:cork, carbon fibers and resin. Evidently, cork is one of the most environmentally-friendly materials as it does not affect it negatively. The cork forests act as CO_2 sequestrators and the fact that it is extracted for commercial purposes actually benefits it as the extraction promotes cork growth and further CO_2 sequestration. Recycling of cork is also quite important so that the carbon dioxide release to the atmosphere is delayed. The cork sector is very self-sufficient throughout its life cycles with very low emissions during the industrial treatment and almost waste-free. All the extracted material is used and reused in cork agglomerates and even waste powder can be used in energy production through combustion. It is important to advertise about the possibility of recycling cork specially when concerning the cork stopper industry that represents more than 70% of the overall market [23]. The extraction of the raw cork is one of the stages that burdens the most the environment, accounting for around 190kg of CO_2 per tonne of raw cork extracted. On the other hand, the ability of carbon fixation by cork oak forests greatly reduces the environmental impact of the industrial activity related to this sector.

According to a study on this matter in Catalonia, these forests fix around 2.9 tonnes of CO_2/ha/year and in drought years may rise to about 3.2 tonnes of CO_2/ha/year. When the cork is extracted and processed into products, some of this carbon will be released back into the atmosphere at the end of life of this product however this percentage is not particularly significant as the cork stripped represents a small amount of the total fixed carbon in each tree. Overall, it can be concluded that the usage of cork has great environmental value mainly due to its very low carbon footprint potential, contributing for the preservation of forest and this particular ecosystem and for the economic development of rural, often poorer regions [41]. Regarding the production of CFRP, it is quite an energy intensive process that will have both consequences in terms of energy used in the facilities and in greenhouse gas emissions, being that for PAN-based carbon fibers, it is estimated that these emissions are around 31 kg CO_2/kg of carbon fiber. The most intensive stage is the transformation of the precursor into carbon fiber and any technology breakthroughs in this matter will be the ones that will contribute the most for the reduction of the environmental impact of CFRP production [42]. It is though important to note that these significant harmful emissions are, in some way, compensated by the smaller fuel consumption in aircrafts due to the weight reduction [43].

4.2   Recycling

Given the growing demand for carbon fiber composites, it is of utmost importance to invest in its recycling and end of life technology, from an environmental point of view. Indeed, the impact of smarter end of cycle treatment for carbon fibers is not only good for the environment but also in terms of resource management and economic impact since recycled materials can be used in non critical applications, solving in a way the problem of lack of supply for the existing demand, and the money spent in legal CFRP landfill disposing can be saved [44]. To comply with international standards like the EU end-of-life-vehicle directive that demand that 85% in weight of each new vehicle from 2015 is reusable or recyclable, there is further need to invest in new processes. When talking about CFRP, it is important to distinguish between a thermoset and a thermoplastic polymeric matrix since the ability of thermoplastics to melt by heating is extremely important from a recycling point of view, however, the preferable resins in the car and aircraft industry, like epoxy, are thermosets and cannot be reshaped after polymerization. The approach to recycle thermoset composites normally follows one of the following: chemical degradation to turn polymeric chains into single chemical components; thermal degradation to turn it into char and energy and mechanical process in order to turn the composite into filler material. Chemical and thermal processes often fall in the category of fiber reclamation processes where the matrix is broken down and the fibers are recovered without significant degradation. These processes, as well as mechanical degradation, follow the scheme in Figure 4.1 [44]. Of course these processes have some disadvantages: thermal degradation leads to reduction in mechanical properties and char deposition and chemical degradation is highly dependable on the resin type. There are several new recycling processes being developed and new products like new epoxy hardeners that work in a different way, being able to obtain recyclable thermosets that can then be transformed into thermoplastics [45].

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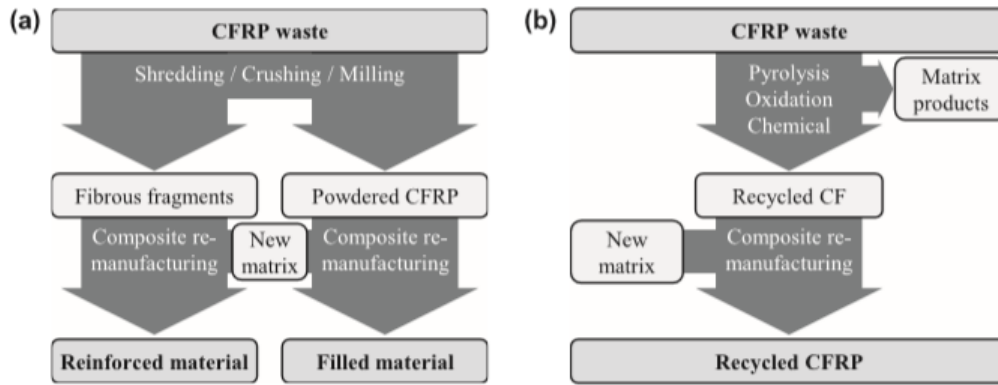
Figure 4.1: Main technologies for CFRP recycling through a) mechanical degradation or b) fiber reclamation [44]

One study points the chemical decomposition of CFRP with supercritical methanol given that the epoxy resin, being soluble by supercritical methanol, separates itself from the carbon fiber and can be reused. Supercritical fluids are defined as fluids and temperatures and pressures above the critical point with a density similar to liquids, viscosity similar to gas, diffusivity and dissolving power. In this case, it was found that the residual ratio, or the percentage of epoxy insoluble by methanol after the decomposition, was dependant on the reaction time and temperature of the experiment, according to Figure 4.2. For this uncatalyzed reaction, it was concluded that all of the epoxy resin was dissolved through this method in 1 hour at a temperature above 270 °C and in 2 hours for 250 °C [46]. However, using this process in a larger scale would not be sustainable in terms of time consumption and energy usage. Regarding the cork agglomerates recycling, the best option would be the mechanical grinding in order to obtain new material for new cork products or for fillers. Besides this, thermal degradation could be used in order to produce energy for other purposes.
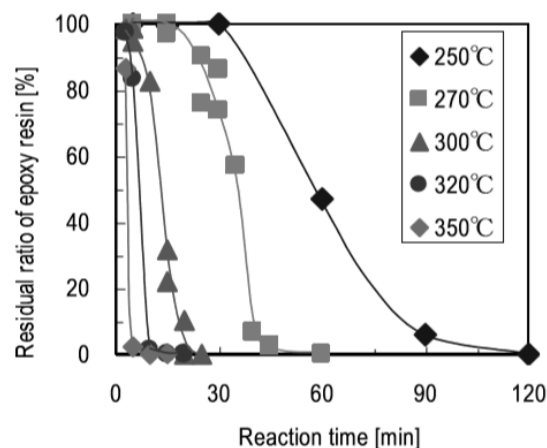
Figure 4.2: Epoxy residual ratio in function of time and temperature with supercritical methanol decomposition [46]

Another study points out pyrolysis as a promising recycling process for CFRP due to its low energy consumption, low cost and good quality of the fibers after the treatment. Through this process, the

CFRP is put in an oven at temperatures higher than 350 °C which causes the macromolecules of epoxy to be transformed into smaller molecules that evaporate and can then be used as energy source for the whole procedure. After the epoxy evaporation, the fibers and pyrolytic carbon remain in the oven and can then be recovered. It is important to note that this process and the overall final quality of the recovered fibers is highly dependant on a set of parameters like oven atmosphere, temperature and heating rate. Studying pyrolysis separately in an air and nitrogen atmosphere, it was concluded that for temperatures between 400 °C and 550 °C, the nitrogen atmosphere allows for a bigger weight loss concerning the evaporation of epoxy however, for temperatures above this range, the air atmosphere allows for oxidation of the pyrolytic carbon and full removal of original matrix. Caution is needed not to allow for oxidation of the carbon fibers at temperatures around 650 °C since this phenomenon will greatly reduce the mechanical properties of the fibers. After optimization of the pyrolysis procedure, first the organic material was removed in a nitrogen atmosphere at 550 °C so that there would be no sudden temperature increase due to the exothermal nature of organic material oxidation. After cooling down, the pyrolytic carbon was then removed by partial oxidation at 550 °C. A tensile strength test showed that the fibers kept most of its properties with a reduction of 3.88 % in comparison with the original tensile strength. Figure 4.3 shows a SEM image of the recovered carbon fibers through this process [47]:
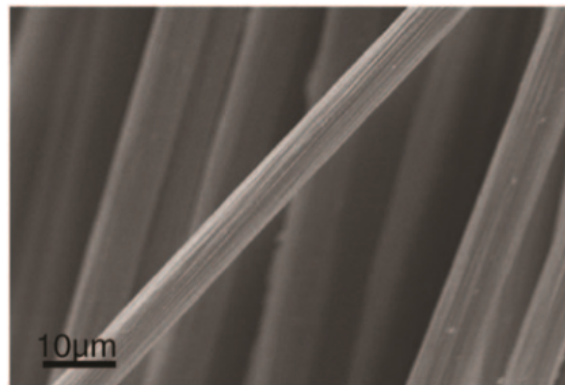
Figure 4.3: SEM image of the recovered carbon fibers through the optimized pyrolysis [47]

Summing up, it is clear that CFRP recycling processes need to be further developed so that the recovered parts can work in near ideal conditions as the original ones. The whole logistical chain of recycling , showed in Figure 4.4, also needs improving and new methods of scrap collection and segregation so that the process can also become cheaper, not expending so many financial resources in aspects like CFRP waste hand sorting for example. Companies like ELG Carbon Fibre Ltd. are already paving the way in this matter, having already established a continuous pyrolysis recycling line at a commercial level with a capacity of 1200 tonnes of recycled fiber per year. Their process allows for a clean carbon recycle, char free and with at least 90% of the properties of the original fibers. This product is then sold at much more competitive prices that fall in the range of one third to half of the price of the original ones [48].

Fortunately, CFRP recycling is becoming a trend globally and major manufacturers are joining the idea. For instance, Boeing began recycling the CFRP from old F-18A and used scrap from 787 fuselage
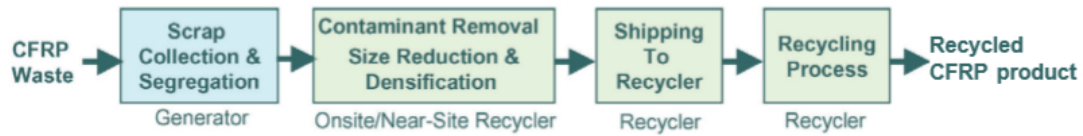
Figure 4.4: Logistical model of CFRP recycling process [48]

tests to design new arm rests. Airbus has committed to reach 85% to 95% of recyclability of its components and materials. And also the University of Nottingham is developing new fiber recycling processes and optimizing them in order to achieve the best recycled material possible [48].

Regarding the direct application on the proposed sandwich composite, one of the best options would be to first use mechanical industrial cutting in order to separate the core from the sheets and then proceed to the recycling processes independently. The core should be subjected to mechanical grinding which would be the simplest recyclable element since it can be easily used for reuse in new cork products or just for fillers. When it comes to the CFRP sheets, chemical degradation for fiber reclamation is the most promising and the one that would be most efficient since mechanically grinding CFRP for filler material is not a suitable option when there are many other fillers in the market for much lower prices. Fiber reclamation by means of chemical degradation is the best option for this part of the sandwich component despite the complexity of it and inherent problems related to the decomposition of the thermoset resin or to the difficulty to completely remove any traces of resin from the reusable carbon fibers.

Chapter 5

Cost Analysis

5.1 Types of costs

To conduct a cost analysis for the development of this new composite material, it is important to first define the different types of costs that must be considered:

- Fixed Costs: these are related to expenses that do not depend on the production, which means that they tend to stay the same even if the production increases or decreases. Some examples of fixed costs are factory building taxes, insurance, machinery depreciation, executives salaries and leasing costs. Since these costs do not change, they cause an increase in the unitary cost of one piece when the production decreases and vice versa. It is important to note though that just because they are fixed, it does not mean that they will remain unchanged forever since changes in machinery, fabric or technology will certainly imply some variation of the fixed costs

- Variable Costs: these costs represent expenses that fluctuate according to the production output which means that they will increase as the production volume increases and vice versa. Some examples of these costs are working hours, maintenance of equipment, packaging, raw materials, transportation of materials, among others.

- Direct Costs: these are directly related to the production of a product or service. These can be linked to materials, labor, transportation and everything that can be directly connected to a certain product.

- Indirect Costs: these are expenses that are not directly linked to a certain product or service. One example may be utilities expenses such as water, gas and electricity used in the factory overall but not directly traceable to a certain activity, product or project.

- Opportunity Cost: this is the benefit given up when a certain decision is made over another one. This is specially important for mutually exclusive cases where the opportunity cost refers to the difference in the returns. The opportunity cost does not appear in the financial statement however it is important in the product management phase. In the case of this composite, the opportunity cost is not relevant since there were no other options being considered against it.

5.2 Cork agglomerate core

For the preparation of this core, cork granules and epoxy resin would be used and it will be assumed a plank of 30cm x 30cm x 3cm, which amounts to a total volume of 2700 cm^3. For the purposes of this study, medium density cork granules are preferable with a density that will be considered of 0.04 g/cm^3 with a price of 4 EUR per kg (Corticeira Amorim). Since the cork agglomerate blocks are the most suitable in terms of shape to the application and since they have a high cork content of 90%, for the plank considered, a total of 97.2g of cork granules would be required.

Additionally, to produce this core and to fill the remaining 10% of the plank volume, epoxy resin would be needed, for a price of 18 EUR per liter (West System) [26]. In this way, for each of these planks, 0.27 L of epoxy resin would be needed.

The total cost for the cork agglomerate cork regarding the raw materials is noted in Table 5.1:

Table 5.1: Overview of costs for the cork agglomerate core

	Price for the plank [EUR]	Price per m^3 [EUR]
Cork granules	0.39	144
Epoxy resin	4.86	1800
Total	**5.25**	**1944**

Taking into account that the cork granules density 0.04 g/cm^3 and the epoxy resin density is 2 g/ml, the total weight for the 30cm x 30cm x 3cm plank core is 637.2 g, which gives a price of 8.24 EUR/kg of cork agglomerate core.

Until this stage, only raw materials have been considered for the analysis of the cork core however, once the mold for the desired shape is concluded, it should be easy to obtain the final core through compression molding or resin transfer molding which are fairly simple processes that are easily available. Vertical integration with the CFRP production could make more efficient the whole process since the machinery needed for the production of the core is most likely available in facilities for the production of CFRP. In this way, costs can be reduced and production can become quicker.

5.3 CFRP sheets

Regarding carbon fibers, it can be more difficult to conduct a cost analysis as most companies keep most of the production process in secrecy. In this case, PAN-based carbon fibers will be the ones considered since they would suit the best the proposed composite material. According to [49], the breakdown of costs for this type of carbon fibers follows roughly the pie chart in Figure 5.1

The different stages of production of the carbon fiber will add to the total cost that is predicted at 19.4 EUR/kg [50]. The PAN precursor is evidently the most expensive part of the production process and it is as well very dependant on the petroleum price which makes the whole cost structure more sensitive to economical and geopolitical factors. The stabilization/oxidation stage is also quite time consuming and financially consuming due to the need of high temperatures for longer periods, representing about 16% of the total cost. It is important to note that the slice regarding the precursor already has in consideration

PAN Based Carbon Fibre
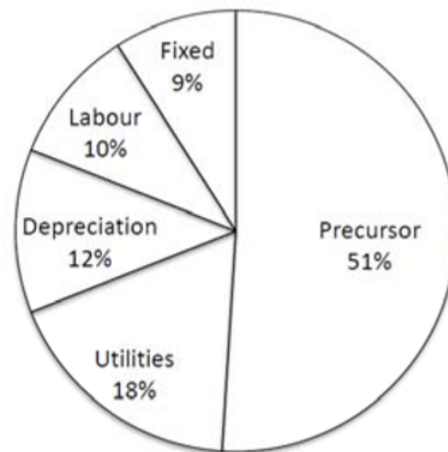
Figure 5.1: Cost breakdown for PAN-based carbon fibers [49]

the spinning of the fibers. Overall, the cost breakdown for each phase of the carbon fiber production can be found in Table 5.2 [50]:

Table 5.2: Overview of costs for phases of carbon fiber production

Process steps	EUR per kg
Precursor and Spinning	10
Stabilization or Oxidation	3
Carbonizing	4.6
Surface Treatment	0.7
Sizing	1.2
Total	**19.5**

An important factor to consider as well in the production is yield which accounts for the weight loss along the process, specially during the carbonizing phase, where all the elements other than carbon are eliminated. PAN-based carbon fibers have a yield normally between 50% and 55% which means that, from 2kg of PAN precursor, one can produce around 1kg of final carbon fibers. Evidently, a lower yield will mean higher costs as more base material would be needed for the same weight goal. For each of the considered planks, the core will have to be covered on both sides by a 30cm x 30cm x 0.2cm sheet which will amount to a total of 360 cm^3 of CFRP sheets for each plank.

For the purposes of this study, a carbon fiber content of 65% in volume is assumed in the CFRP sheets which is a normal value in the industry. Given the normal density of carbon fibers of 2 g/cm^3, there is a need for $360 * 2 * 0.65 = 468g$ of carbon fiber, amounting to a price of 9.13 EUR. To complete the CFRP sheets, the remaining 35% in volume will be filled with epoxy resin, which means that 126 ml or 252 g of this resin will be used, amounting to a price of 2.27 EUR. Taking into account the partial contributions, the CFRP sheets for each plank will have a price of 11.4 EUR. Given that these CFRP sheets total a weight of 720 g for each plank, they will cost 15.83 EUR/kg.

5.4 Energy

Cork has quite a low cost when it comes to utilities and, in the case of this composite, most of the cost will be associated with the production of the CFRP. According to [51], currently and with the mainstream technologies available, the production of carbon fiber has a cost of 1134 MJ/kg which is significantly higher than the utilities usage for the CFRP production itself which is 39.5 MJ/kg. The production of epoxy resin also uses 89.8 MJ/kg. Evidently, the energy use overall will depend on the percentage in weight of carbon fiber and of epoxy resin, as can be seen in Table 5.3. Since the carbon fiber production is so much more heavy in terms of energy use, this percentage will greatly influence the final cost.

Table 5.3: Energy use for different weight balances in the CFRP

% in weight CF	% in weight epoxy	Energy used [MJ/kg]
30	70	442.56
40	60	546.98
50	50	651.4
60	40	755.82
70	30	860.24

Basing this analysis in EU prices, and following the report [52] and Figure 5.2, it can be assumed that the average price for electricity in the EU in 2019 is 0.22 EUR/kWh or 0.061 EUR/MJ, since $1kWh = 3.6MJ$. With this information, Table 5.3 can be complemented with the cost information in Table 5.4:

Table 5.4: Energy use and overall cost for different weight balances in the CFRP

% in weight CF	% in weight epoxy	Energy used [MJ/kg]	Cost [EUR/kg]
30	70	442.56	27
40	60	546.98	33.37
50	50	651.4	39.74
60	40	755.82	46.11
70	30	860.24	52.47

Given that the assumed densities for both the carbon fibers and the epoxy resin are the same, the percentage in weight will be equivalent to the percentage in volume. In this way, and given the 65% of carbon fiber in the CFRP sheets, the energy cost for its production will be of 49.29 EUR/kg of CFRP or 35.49 EUR/kg of sandwich panel.

Since the energy used for the production of the cork agglomerate core is very reduced in comparison with the energy cost for CFRP production, the analysis will consider an addition of 10% the the energy cost to account for the cork agglomerate core and for the energy used for the final assembly of core and sheets. Summing up all the contributions the total cost breakdown can be found in Table 5.5. Note that the total weight for the proposed dimensions plank is $637.2 + 720 = 1357.2g$.

Table 5.5: Total cost breakdown for the proposed sandwich composite

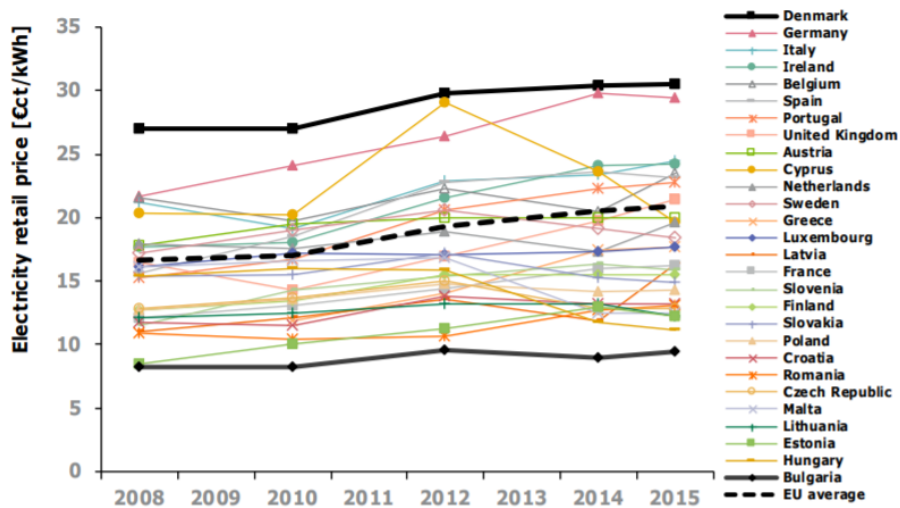| Contribution	Price [EUR/panel]	Price [EUR/kg of sandwich composite]
Cork agglomerate core materials	5.25	3.87
CFRP sheets materials	11.4	8.4
Energy usage for CFRP production	35.49	26.15
Energy usage for core and sandwich production	3.55	2.62
TOTAL	55.69	41.03

Figure 5.2: Electricity prices throughout the EU in the recent past [52]

5.5 Equipment

In order to produce both the core and the sheets, some basic equipment needs to be available, being that one can choose between different equipments according to its advantages and disadvantages. Regarding Resin Transfer Molding, the equipment and price may vary significantly according to its capabilities that can include the ability to store binder and catalyst, adjustable mixing ratios or resin temperature and pressure monitoring. The pressure of resin application and size of the storage unit will also have some implication on the price. For example, adding a vacuum chamber to prevent air from entering the materials would cost an additional 40.000 USD while pressure transducers to maintain predetermined pressures in the pumps would add between 5.000 and 10.000 USD. Bigger heated resin containers also add a cost where a 7.5 L container adds 8.000 USD and a 19 L container adds 9.500 USD. In general, the total initial investment for this kind of Resin Transfer Molding equipment will vary between 5.000 and 100.000 USD. Normally, pneumatic flow controlled devices are more expensive than the electrical controlled ones [53]. RTM may be one of the best options as it presents very good results both for the CFRP production and the cork agglomerates. The mixing ratios allowed, as well as the injector shot sizes also greatly influence the final price as illustrated in Figures 5.3 and 5.4, respectively:
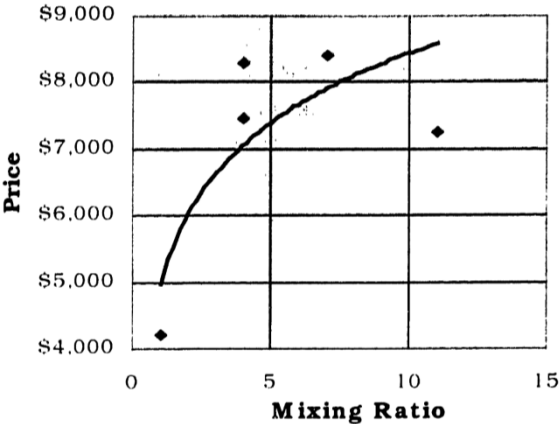
Figure 5.3: Difference of prices for different mixing ratios dispensers in non-automated RTM equipment [53]

When it comes to pultrusion, the investment may be significantly higher, ranging between 100.000 and 400.000 USD. These equipments are quite large and can occupy very large areas of the factory. The pultrusion equipment is very long as it includes several sub sections like dry fibers storage, resin bath station, heated forming die with heating and cooling section and pulling mechanisms. Prices depend mainly on 3 factors: part envelope size, pulling strength and whether the pulling mechanism is continuous or reciprocating where the continuous ones are the most expensive as showed in Figure 5.5. The pulling strength of the mechanism will also influence the price according to Figure 5.6 however it is important to note that, the bigger the piece size, inevitably the higher will have to be the pulling capacity in place [53].

For autoclave equipment, the price range is quite wide ranging between 80.000 USD and 2.500.000 USD depending on several factors like temperature range, pressure range, digital monitoring, heating
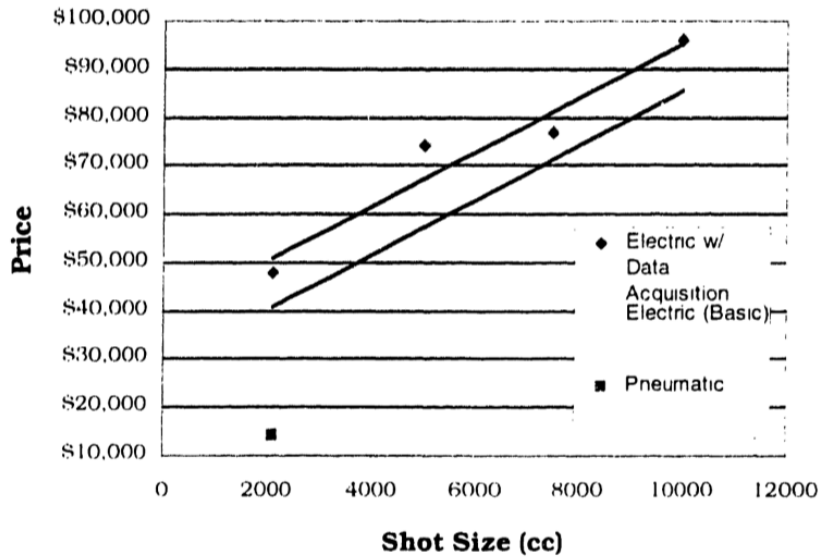
Figure 5.4: Difference of prices for different shot sizes dispensers in automated RTM equipment [53]
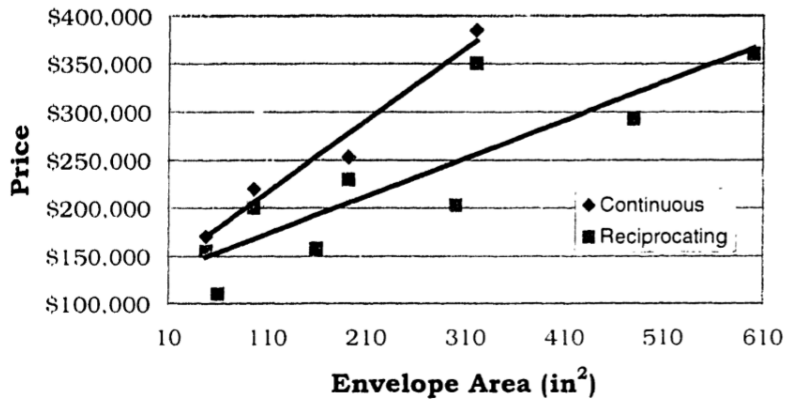

Figure 5.5: Difference of prices considering type of gripping mechanism and piece envelope area [53]
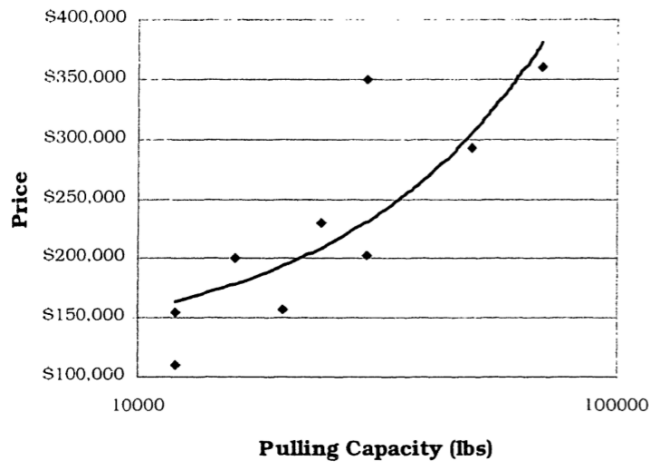

Figure 5.6: Difference of prices considering pulling capacity in pultrusion equipment [53]

and cooling rates, size, among others. When it comes to curing, pressure varies between 5.5 bar and 7 bar and temperature between 120ºC and 450ºC however these autoclave ovens are capable to achieve even greater temperatures and pressures. For pressurization, normally nitrogen or carbon dioxide are used while gas is used to heat higher capacity autoclaves and electricity for smaller ones. One of the main factors that greatly contributes to the increase of the final price is the addition of fully automated temperature and pressure control systems [53]. In Figure 5.7 the dependence of autoclave prices on the pieces volume can be observed:
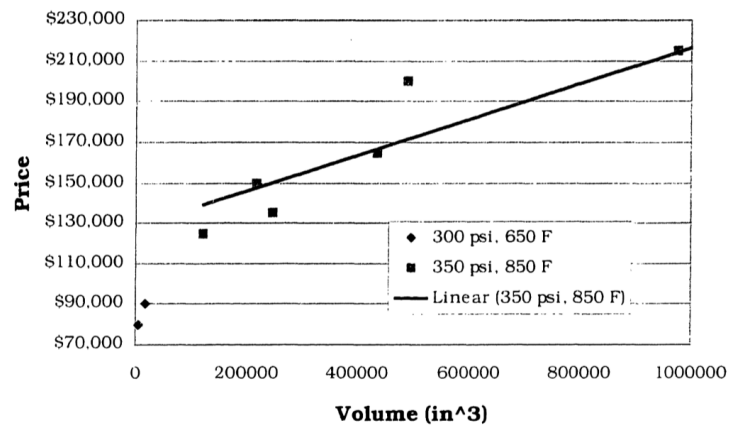

Figure 5.7: Difference of prices considering volume pieces in autoclaves [53]

One of the materials used that is used in this type of fuselage applications is PMI foam mainly due to its adaptability to complex shapes, ability to support cover layers like prepregs, resistance to corrosion and moisture [54]. The minimum density for PMI foams is 0.07 g/cm^3 which is higher than the density for the cork granules (0.04 g/cm^3) but lower than the total density of the proposed sandwich panel estimated at 0.50 g/cm^3.

As mentioned in section 3.2, cork agglomerate cores respond better to impact, sustaining less damage. Moreover, cork agglomerate cores present much better flexure after impact performance which is an important feature in any component of the fuselage [35]. The addition of the CFRP sheets to the core would assure an even better performance with higher resistance and corrosion and fire resistance while maintaining low weight, allowing for savings in weight in some fuselage reinforcements.

According to Qingdao Regal New Material Co., the price for PMI foam is estimated around 15 EUR/m^2 for sheets with a thickness of 3 mm. This would mean that, for a PMI foam sandwich core, as it is usual the case, with the same dimensions as the proposed one, the price would be of 45 EUR. This price is much higher than the price estimated for the cork agglomerate core of 5.25 EUR, which further testifies for the interesting economical opportunity in this new sandwich composite. The comparison is made between the cork agglomerate and PMI foam as cores alone because they would always have to be covered by sheets of a more resistant material such as CFRP.

Summing up, considering the relative prices and the expected behaviour of the new proposed sandwich composite in the inner fuselage of aircrafts, there is a need for further studying on its real performance to assess whether the possible cost savings do not compromise its function.

Chapter 6

Conclusions

After this comprehensive overview of a sandwich composite material development constituted by a cork agglomerate core with CFRP sheets for application in the inner skin of the fuselage, it can be concluded that this material is suitable for further research with the aim of being used as a consistent alternative to common materials such as PMI foams. The unique properties of cork combined with carbon fiber result in an extremely light material with very good mechanical properties that could be put to good use in the aeronautical sector. Since one of the biggest challenges in the sector is to find lighter solutions with up to standards and compliant behavior, this is without a doubt one of the options to explore further.

This sandwich composite would be specially suitable for application in non structural inner fuselage panels with function of thermal and acoustic insulation, contributing to the overall comfort of the passengers and crew. Moreover, testing shows that this new sandwich composite could mechanically outperform PMI foams normally used in these applications.

Today's manufacturing techniques, together with testing mechanisms and computational tools can ease the path for the full development of the new composite. Particularly, compression molding seems like a suitable candidate for its manufacturing given its high reproductibility capacity and good final mechanical properties.

To take into account the environmental sustainability in new product developments for aircrafts, the implementation of recycling processes and sustainable materials is essential. The sole use of cork in this new composite would significantly reduce the environmental impact as it is a much greener material than most of the ones used in the aeronautical industry nowadays such as aluminum, steel or titanium. The use of cork would also be profitable for local and regional economies due to increased demand in areas as the southern Iberian Peninsula and other areas of southern Europe. Regarding the CFRP sheets that are more environmentally harmful, there is a need for further developments in the area of chemical degradation in order to obtain reusable fibers without significant damage.

Cost-wise, the new sandwich composite core presents a lower cost than PMI foam, a material normally used as core is similar panels for this application in the fuselage inner skin. Regarding the overall cost of the panels, the greater cost percentage would be related to the CFRP raw materials and the energy needed for its production while the cork agglomerate core represents only a small percentage of

the total cost.

Summing up, the proposed sandwich composite seems to be an innovative option to consider for application in the inner fuselage, presenting better mechanical properties than industrial foams sandwich composites and assuring as well the functions of thermal and acoustical insulation. Furthermore, besides presenting low density for effects of aircraft weight reduction, it assures a very good environmental sustainability due to its use of cork in the core.

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Appendix A

ASTM Testing Standards

In the engineering field, international standards are of upmost importance as they set the norms and procedures for a variety of procedures from manufacturing to quality control. Below, a list is presented with some important ASTM standards to be considered for the sandwich composites:

- **ASTM D256 - Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics**: used for determining the impact thoughness through the Izod Test

- **ASTM D6110 - Standard Test Method for Determining the Charpy Impact Resistance of Notched Specimens of Plastics**: used for determining the impact thoughness through the Charpy Test

- **ASTM D3878 - 18 - Standard Terminology for Composite Materials**: basic terminology used in composites both in the industry and comercially

- **ASTM C271 / C271M - 16 - Standard Test Method for Density of Sandwich Core Materials**: provides a method to determine the density of the core material of a sandwich structure

- **ASTM C273 / C273M - 18 - Standard Test Method for Shear Properties of Sandwich Core Materials**: method to determine shear properties of sandwich structure by applying loads parallel to the facings and registering force-deflection data

- **ASTM C297 / C297M - 16 - Standard Test Method for Flatwise Tensile Strength of Sandwich Constructions**: used to determine the strength and integrity of the core-to-facing bonds, its stability and load transfer between the two components

- **ASTM C365 / C365M - 16 - Standard Test Method for Flatwise Compressive Properties of Sandwich Cores**: method to determine the compressive strength and modulus of a sandwich structure through a force-displacement curve

- **ASTM C394 / C394M - 16 - Standard Test Method for Shear Fatigue of Sandwich Core Materials**: study the effect of repeated shear stresses in the core material of the structure

- **ASTM C480 / C480M - 16 - Standard Test Method for Flexure Creep of Sandwich Constructions**: method for a creep test applying a constant load for a certain period of time, obtaining deflection data over time and establishing a creep rate

- **ASTM D6772 / D6772M - 16 - Standard Test Method for Dimensional Stability of Sandwich Core Materials**: heat can compromise the dimensional stability of a structure and this method can be useful to analyze possible problems regarding the wanted dimensions

- **ASTM F148 - 13 - Standard Test Method for Binder Durability of Cork Composition Gasket Materials**: measurement of the chemical cure of binding agent used in cork compositions

- **ASTM F152 - 95 - Standard Test Methods for Tension Testing of Nonmetallic Gasket Materials**: determination of tensile strength for this type of materials where cork is included in Type 2 materials

- **ASTM F36 - 15 - Standard Test Method for Compressibility and Recovery of Gasket Materials**: determination of short-time compressibility and recovery at room temperature for cork

- **ASTM E289 - 17 - Standard Test Method for Linear Thermal Expansion of Rigid Solids with Interferometry**: determination of coefficient of linear expansion in solids composed of different materials using a Michelson or Fizeau interferometer

- **ASTM E2533 - 17e1 - Standard Guide for Nondestructive Testing of Polymer Matrix Composites Used in Aerospace Applications**: review about non destructive testing techniques that are used in the aerospace industry, and its treatment of data to determine fitness for use

Appendix B

Logistics and Supply Chain

The development of a new product also involves the development of a supply chain with certain logistics that allow for a people and machines' system to be created that can effectively serve the client's needs both in terms of costs and time. These logistics have to be carefully studied and determined as they involve not only the supply of raw materials as the management of these materials in the factory and later distribution of the final product to the customers. There is indeed a need for integration in the whole process of information, transport, inventory, warehousing, shipment and security as can be seen in Figure B.1. Obviously, in the case of a new material, these logistics can always be adapted form other products with some minor changes. Inside the EU, due to the assurance of the single market, logistics costs declined greatly specially due to the reduction in transportation between EU member states. According to the EU White Paper of 2001 and 2011, there is a need for further integration of all modes of transport, not only focusing on road transport which can be one of the most harming in the light of sustainable development [55].
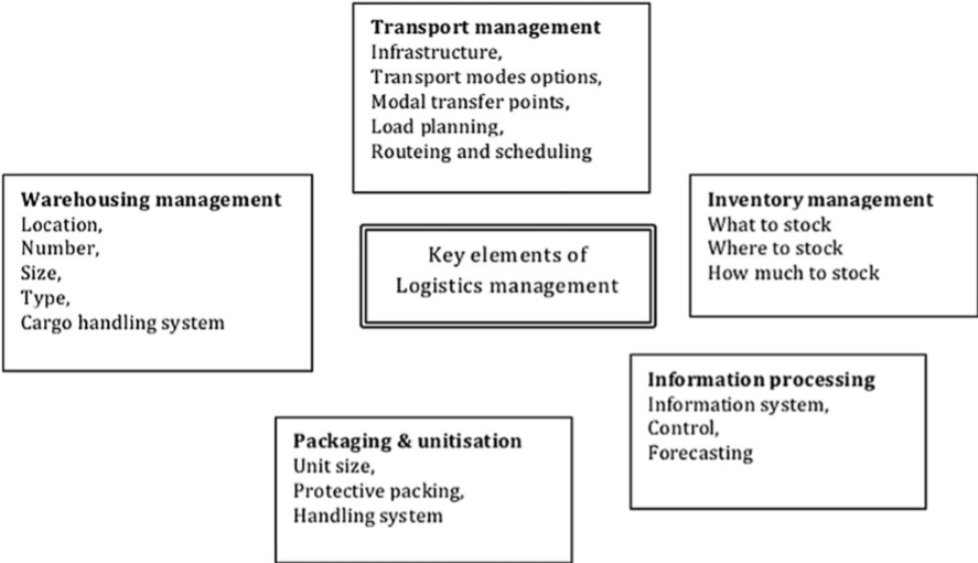

Figure B.1: Pillars of integrated logistics [55]

The industry of new materials is quite sensitive to many external and technical factors such as unforessen innovation, competing technologies, patents, rise in others materials' prices and world's economy growth rate. Like any global market, this market as well presents a cyclical pattern of growth and recession: growth acceleration leads to overcapacity and oversupply, leading to a decline in prices, substitution of materials and industry regeneration. The composites industry has already proved its worth and its technical applications which means that, despite the normal cyclical periods, it is an industry that will continue to flourish. Being so sought for, it is normal that companies in this sector practice economies of scale where volume is the most important. This does not mean that there is no space for niche and specialised submarkets given that usually they are of higher value and can be easy to get into when the area of the industry is more fragmented [56].

The aerospace market has been the most important sector for carbon fiber and CFRP composites, representing around 45% of the carbon fiber demand in 2012. According to Figure B.2, as of 2012, composite materials represented around 3% in weight of the aircrafts' material demand; this represents around 16.300 tonnes of carbon fiber which, given the lightness and price per tonne of the material, represents quite a significant volume and also profitable returns. Statistical studies also indicate growth rates in the double digits mark, pointing out that, despite normal fluctuating movements, this is clearly a market that tends to continuosly grow [57].
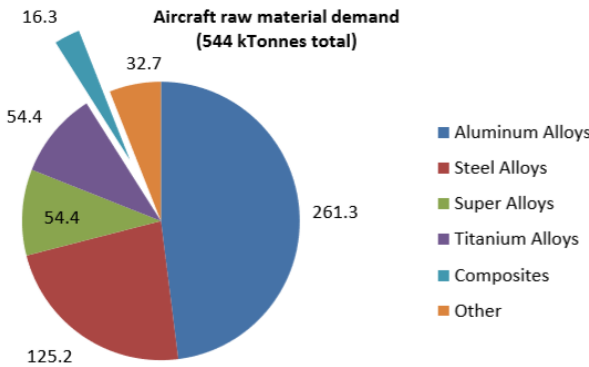

Figure B.2: Distribution of raw materials demand for aircrafts [57]

The aerospace industry remains one of the most controlled and with tighter security restrictions and this will inevitably lead to higher prices for both CF and CFRP however this has not been stopping this industry from investing more and more in these materials, even more than all other industries, as can be infered from Figure B.3 where demand has been and is predicted to continue growing [57].

Regarding carbon fiber, small tow carbon fiber manufacturing used in aerospace applications is centered around a handfull of companies that dominate this market nowadays - Toray, Toho Tenax, Mitsubishi Rayon, Hexcel, Cytec and Formosa Plastics. Toray, based in Japan and major supplier for Airbus and the Boeing 787, is without doubt the lead manufacturer with 50.000 tonnes of production per year expected in 2020, having even developped the supply chain for finished CFRP and pre-pregs in Japan, France and the United States, vertically integrating their production chain, meaning that the main company owns several different businesses in different territories that take part in different stages
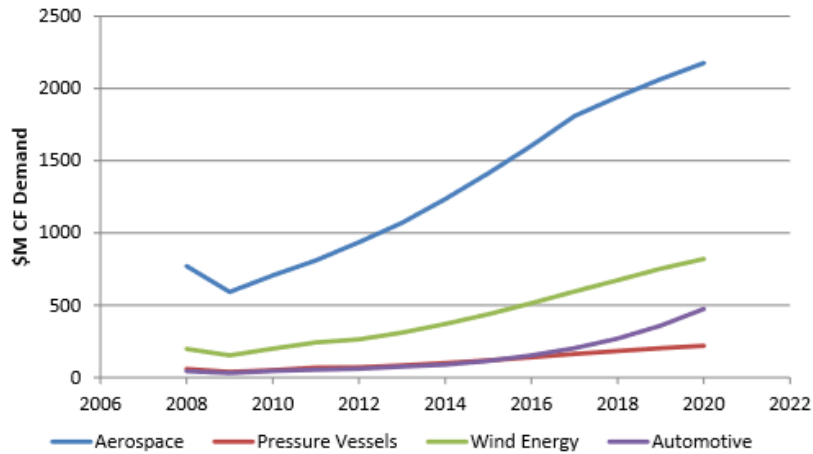
Figure B.3: Demand of carbon fiber by sector [57]

of production. Toho Tenax has a 2020 expected capacity of 18.900 tonnes per year with most of the production centered in Shizuoka, Japan, and it focuses on thermoçlastic CFRPs for the Bombardier C series and the A380. Mitsubishi Rayon has a supplier contract with Airbus regarding the A380 and it also has its production centered in Japan with a predicted 2020 capacity of 14.300 tonnes and it specializes in the production of acrylic fiber. Hexcel is a smaller firm with a predicted capacity of 10.000 tonnes per year, based in the US and driven mainly by contracts for the A350 and A380. Cytec is also based in the US with a smaller predicted capacity of 6.000 tonnes per year and specialized in prepregs which are used in the Boeing 787. [57].

Regarding the cork supply chain, this raw material has to go through different stages until it arrives to the final consumer. The first stage consists of forest management which englobes several operations such as cleaning of forest area, planting and fertilization, substitution of dead plants, manual cork extraction, transport of cork planks and of the workers, field recovery. Secondly, cork has to be prepared for use and this stage includes piling the planks, stabilizing them in open air for six months so that the ideal moisture content of 6%-10% can be achieved, cork boiling, second stabilization for flattening, manual selection of planks and defect inspection. Finally, the planks have to be cut and sliced into the desired dimensions, the cork dust has to be removed and the final cork piece has to be disinfected with hydrogen peroxide or paracetic acid [58]. The Iberian market remains the top exporter of cork and so, most of the cork treatment stages tend to take place in these territories so that afterwards, the planks can be shipped to the final manufacturing destination. The map in Figure B.4 shows the flow of cork from the Iberian market to their destinations. Portugal is also the main exporter of the agglomerated cork that would be more suitable for this kind of composite and it also requires passing through the refered stages and through the grinding to the desired particle size [22].

In order to control the production and inventory needs for this new material, it is essential to follow some kind of material requirements planning (MRP) which plans both the production and inventory based on the finished product demand and clients' needs like in Figure B.5 [59]. The base of any MRP system is the requirements (demand) of the component which can vary quite significantly between peri-
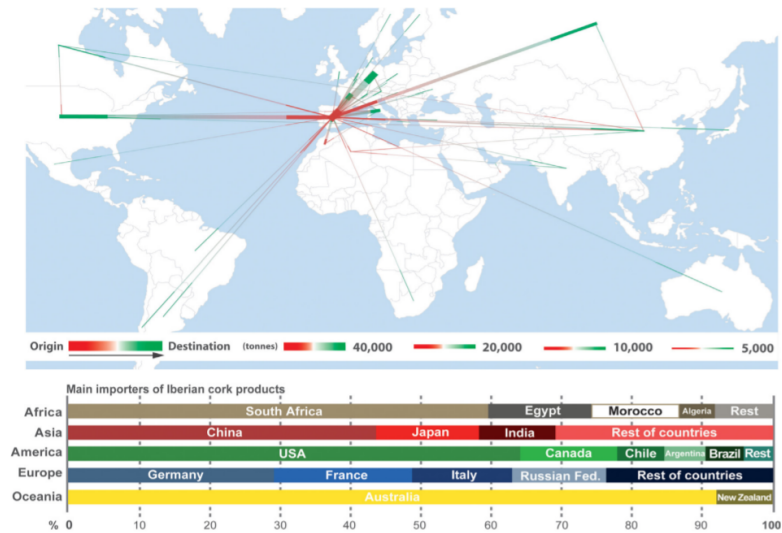
Figure B.4: Global distribution of Iberian cork [22]

ods in many manufacturing industries and this effect can be measured through a coefficient of variation that increases with increasingly lumpy demand. Considering the gross requirements, inventory and scheduled receipts in one period, the projected inventory can be determined for the next period and the system can be adapted for a safety stock (inventory). These MRP systems also have to take into account fluctuant demand as it will affect lead times (time required to manufacture an item) and delivery schedules to the client. Demand from the final client can also be very fluctuant and this can be seen often when a demand that was scheduled for a certain period arrives on a different period sooner or later than predicted. The supply of lower level material, like agglomerated cork or carbon fibers in this case, can also vary due to failure by the materials providers, resulting in further uncertainty in complying with gross requirements [60].
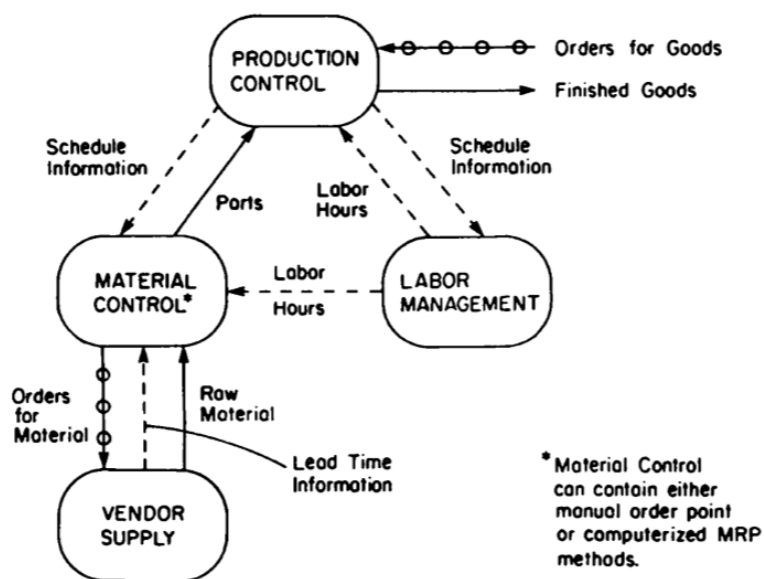

Figure B.5: Organizational diagram of MRP [59]

Appendix C

Industry and Innovation

Innovation in engineering is a constant need in order to solve different problems, develop new ideas and products and contribute for the advance in technology and scientific knowledge sharing. In the manufacturing industry, there are several possible sources for this innovation that can be analyzed and studied. Looking from a firm perspective, internal information and in-house capabilities provide the primary source for innovation while external factors focus on customers, suppliers, competitors, industrial fairs and professional conferences. Design in engineering has always been a matter of being creative in order to fulfill the needs and requirements of the final user and this can often be achieved by combining different technologies already in use. The innovative process is almost always iterative, relying constantly on feedbacks and tests to reorganize the process and optimize the final product. The Voice of the Customer is often one of the most important sources for stimulating and guide the search for innovative processes and products. Often, design decisions have to be made as an experience based on personal preferences and past experiences given the small amount of information and high uncertainty regarding the results. ICT tools such as CAD software, simulation software, intranets and online databases have become some of the main paths for solving problems, improve design techniques and work communication [61].

A study on innovation in the Italian manufacturing industry concluded that this phenomenon is very heterogeneous and therefore hard to quantify. Many times, it is also difficult to identify innovation itself since these technological activities, that can be tangible or not, can occur outside of the market sphere. In this particular country case, the industrial sectors present the bigger percentage of sales and employees of innovating firms, specially aerospace, office machinery, radio TV and telecommunications which are sectors with high technological opportunities. Innovation in the industry is strongly influenced by the size of the firm mainly due to the financial capabilities when it comes to R&D expenses and investment. Bigger firms tend to generate new technology internally while smaller firms tend to innovate by using the external market to acquire new machinery, technology and plants [62]. According to a study on the UK market, firms are spending less in internal R&D, innovating by drawing expertise from external sources and relying on the heavy mobility of knowledge workers of today's working culture [63].

C.1   Research and Development

When developing a new product, it is always essential to invest in R&D whether it is related to the product itself or to the process. Technological progress has always been dependant on total R&D efforts and investment however the way these different investments are channeled through has been a theme for discussion. Depending on the industry, investment can be more directed to the development of the product or of the process. If developped by an engineering firm, this new material would also be subjected to extensive R&D research due to being a novelty in the industry. Larger firms would have it easier financially since they would have greater output and could spread their costs more easilys: the advantage of cost spreading related to large firms is specially noticeable when it comes to the process R&D compared to the product R&D [64]. Product and process R&D reinforce each other as one leads to the development of the other. Normally, process R&D allows for bigger price to cost margins since the costs of production are reduced while product R&D allows for the charging of higher prices by investing in costumer needs and awareness for that product. Since the total profit is equal to the number of products sold times the price to cost margin, it is obvious that both types of R&D are essential to its success. In the development of a new material, the firm developping it has to go through several investment stages: initially, product R&D is evaluated so as to determine the degree of differentiation between products; secondly, process R&D is evaluated so that, in the end, the new products can compete in the open market [65].

In an age when innovation is becoming everytime more open, it is important for firms to cooperate when it comes to sharing of knowledge in order to make innovation more accessible. Using this concept, time to market of a product reduces considerably and the efficiency of R&D is much clearer. Regardless of all the benefits, there are significant barriers such as higher coordination costs, loss of knowledge, difficulty in finding the most suitable partners, insufficient time and financial resources. It is essential to find the right balance in each firm between closed and open innovation: too much openness can put boundaries on the success of long term innovation and having too much closed innovation could compromise the serving of demands for shorter innovation cycles [66].

When a new project is undertaken, it is important to understand before the market, technology, costs of production and process as well as the factors that could determine the success or failure of this new introduction. According to this study, the nature of the innovation, of the market and of the technology are the three major groups of variables that influence most the outcome of a certain new product. The nature of the innovation concerns whether it is incremental, where only minor changes are made in some factors without any major changes to the basic technology and configuration; or radical, where the technology used has to be completely different from the one that is established. In this case, a new composite of this type would present an incremental innovation as most of the technology needed is already in place and only some small details would have to change in order to achieve the best material. The nature of the market refers to whether it existed already or it is being created from scratch and in this case, the composite materials market is already well established so the uncertainty is not very high. Regarding the technology issue, when evaluating a new project,

one should consider whether it involves high tech or low tech. In the high tech field of composites for engineering, technology is always changing and developing and with it new products are constantly emerging. Due to this situation, the possible applications and customers of the new product may still be poorly defined and competition is normally fiercer as there is a higher and constant input of new products and innovations [67]. The interface between R&D and marketing, which is the unity among its subsystems, is also crucial in the product development process and it will be conditioned by the firm's strategy and the uncertainty in that specific market. The more participative the management style is and the more informal and decentralized the firm is, the better the understanding between R&D and marketing. Using multidisciplinary teams, involving marketeers, scientists, engineers and management people, is crucial in what regards new product development [68].

When it comes to the specific case of aerospace industry, composite materials are taking the lead when it comes to NPD projects due to their increased strength and reduced weight. For instance, Bombardier is approaching technology as a mean to support NPD in an evolutionary way, adapting solutions in order to reduce possible extra costs and reduce risk and aligning as much as possible the requirements of the NPD with the existing potential and capability. Automation is an essential factor specially when it comes to designing pieces with complex shapes and that is why this specific company is investing quite a lot in digital manufacturing and in Computer Aided Engineering softwares. The flow diagram, according to Bombardier, for a composite NPD should follow the one in Figure C.1. The leaders in this industry like Airbus and Boeing are investing extensively in composite structures however they do not cooperate directly significantly between them due to competitive competitive and intellectual property related issues, however, they share knowledge through mutual equipment manufacturers, sub suppliers and out of sector partnerships. University partnerships are of added value since they allow for technology and knowledge transfer across many projects besides some reluctancy when it comes to intellectual property and the publishing of findings [69].
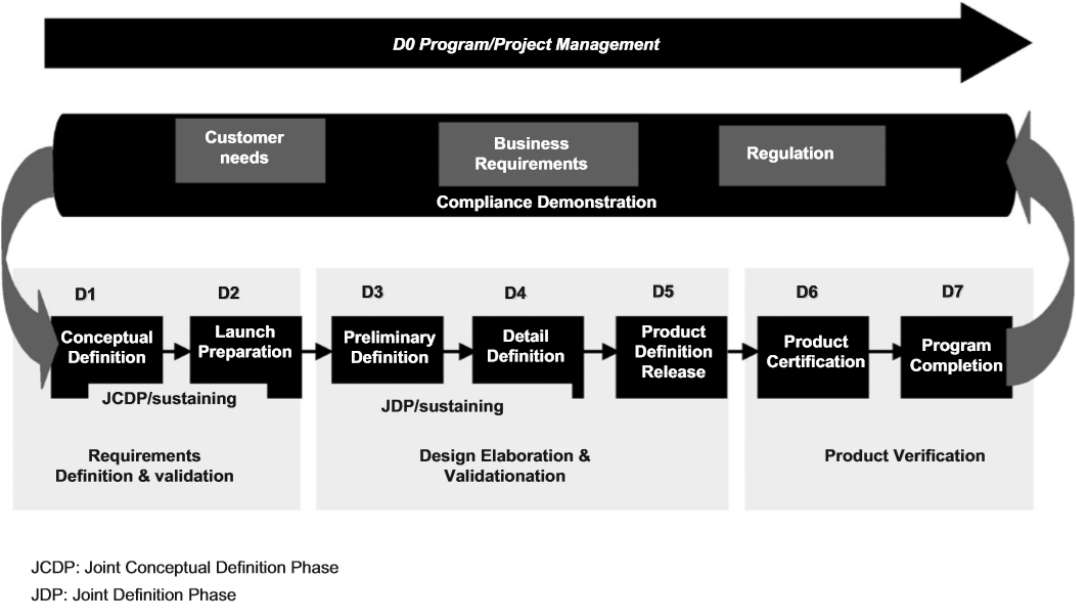

Figure C.1: Flow diagram for a Composite NPD [69]

C.2   Patenting

Any firm, when developing a new product, hopes to make a profit out of their innovation that makes it worth for the product development risk and expenses. Patents are one of the most classic ways governments have found to allow firms and innovators to maximize their profits. It is essential that a candidate for patent protection meets the criteria of novelty, non-obviousness and utility. Since patents give the owner legal protection regarding their product, this can lead to a monopoly of a product for a certain period of time which means that the firm can charge higher prices. Despite this, there should be limits to the price imposed as, the higher it is, the more captivating will be for other firms to try to design around the patent through some modifications or infringe the patent as long as the the benefits involved exceed the risks of doing so. One should also pay special attention to which are the countries where the product should expect more attention and where it can achieve its full potential as there is no such thing as an international patent. Patents are valid in a national context and each new domestic market would require a new patent and more expenses and time consumption [70]. Stronger patents encourage licensing, which is the selling or buying of the patent rights, since it makes it more difficult for others to try to go around the patent and free ride on the right to produce something or use a certain technology. Licensing allows for a calm transfer of knowledge without aggressive competition, discouraging as well additional research on a certain patent as, many times, cumulative modifications to the base science of a patent can be a way of going around it. Besides that, when the knowledge patented is very technical, scientific and easily described in written form, designs or algorithms, it is better for licensing since it is easier to transfer and the patent becomes better protected since it is clearer what is being described. When thinking about licensing a patent, a manager should evaluate if the revenue from the licensing fees is higher than the loss of profit from increased market competition, the so called rent dissipation effect. If a patent is strong, the revenue will be higher as it will be extremely difficult for the invention to be copied and the original owner of the patent will more likely be able to maintain the monopoly of the invention. Furthermore, the rent dissipation effect diminishes if the buyer of the patent operates in a distant market whether it is geographically or in terms of operating sector. When a material becomes more complex, so does the amount of technologies involved in the process of producing it which may mean these technologies patents ownership is spread across different companies which might or not be rivals. In a market filled with institutions or companies, patent licensing is more likely as well, specially if these are small firms or research centers [71].