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Bachelor degree in Materials Science

Hot forming thermal cycle and material exposure effect on prepreg materials properties

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À família Correia.

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"Put your desk in the corner and everytime you sit there to write, remember yourself why it isn't in the middle of the room. Life isn't a support system for art. It's the other way around"

- Stephen King

Abstract

Since its first use on Edison's incandescent lamp, carbon fiber has been studied and developed into an important resource in industry. This material is used in many forms but mainly in fiber rolls or tapes and is usually impregnated with resin (prepregs). As such, using ATL (Automated Tape Layup), AFP (Automatic Fiber Placement) or Hand Layup, these are laminated in molds and then may go through hot forming process and/or autoclave process curing. As this material has a time interval which can be used until it degrades its mechanical and processability properties, since the curing process starts when the CFRP is impregnated and the curing process never ceases. Hot forming is being focused since temperature is a major factor for curing speed. Therefore, a test proposal was made to evaluate the effect of hot forming thermal cycle and material exposure in the characteristic and function of the cured laminates. The work developed in this thesis should clear out that ATL material is not suited for exposure conditions while AFP material is capable of tolerate the exposure conditions proposed and be processed through hot forming.

Keywords: hot forming, carbon fiber, exposure conditions, aeronautics, prepregs, ageing.

Resumo

Desde o seu primeiro uso na lâmpada incadescente do Edison, a fibra de carbono tem sido estudada e desenvolvida de forma a ganhar um relevo na indústria. Sendo principalmente usado em forma de rolo ou fita e impregnado com resina (prepregs), apresenta-se de várias formas. Como tal, o material é laminado através da ATL (Automated Tape Layup), AFP (Automatic Fiber Placement) ou laminação manual em moldes, podendo passar pela conformação a quente, e curados através do processo de autoclave. Como este material tem um período de fabricação antes de perder as propriedades mecânicas e de processabiliadade, tendo em conta que a cura dos CFRP começa a partir do momento em que foi impregnado e não para, o processo de conformação a quente é focado devido ao facto de a temperatura ser um factor importante para a velocidade de cura. Sendo assim, uma proposta de ensaios foi feita para avaliar o efeito do ciclo térmico da conformação a quente e da exposição de material na funcionalidade e atributos dos laminados curados. O trabalho executado nesta tese consegue demonstrar que o material usado para ATL não é desenvolvido para sobreviver a um grande envelhecimento, ao contrário do material para AFP que é capaz de tolerar as condições de exposição propostas e passagem pelo ciclo térmico da conformação a quente.

Palavras-chave: conformação a quente, fibra de carbono, condições de exposição, aeronáutica, prepregs, envelhecimento

Glossary

Armalon	Teflon coated fiber-glass release film or peel-ply.
Hot Forming	Forming process of uncured laminates using heat and pressure.
out time	Limit exposure period in which a perishable material could be left out of its storage recommended condition, which is accumulative and the total amount of time the prepreg stays out of its storage recommended condition shall be recorded until it reaches the limit stated by the supplier.
prepregs	Carbon fiber material that has been impregnated with resin previously by the supplier to facilitate and improve the manufacturing process.
Shelf life	It is the period of time from the manufacturing date, in which the material is packed and stored under some specific conditions in order to keep its physical and chemical properties adequate for use.

AFP	Automated Fiber Placement.
ATL	Automated Tape Layup.
CFRP	Carbon Fiber Reinforced Polymers.
DMA	Dynamic Mechanical Analysis.
DSC	Differential Scanning Calorimetry.
FO	Foreign object.
FTIR	Fourier Transform Infrared.
ILSS	Interlaminar Shear Strength.
ILTS	Interlaminar Tension Strength.
NDT	Non Destructive Test.
RTA	Room Temperature and Ambient conditioning.

Sign	Description	Unit
E_A	Activation Energy	$kJmol^{-1}$
ψ	Angle from horizontal of the specimen legs in degrees	º
E^*	Complex Modulus	MPa
$\tan\delta$	Delta tangent	º
D	Diameter of roller supports	mm
T_g	Glass transition temperature	C
$H(t)$	Heat of the reaction at time t	
dx	Horizontal distance between loading bars	mm
r_i	Inner specimen radius of curved segment	mm
E''	Loss Modulus	MPa
t_i	Measurement "i" of the panel's thickness	mm
T_p	Nominal ply thickness	mm
T_n	Normalized ply thickness	mm
T_{pi}	Normalized ply thickness of the "i" panel	mm
n_m	Number of measurements	
n_p	Number of panels	
N_p	Number of plies on the panel	
r_o	Outer specimen radius of curved segment	mm
P	Pressure applied by the ILTS support	MPa
$\frac{d\alpha}{dt}$	Rate of cure	
$f(a)$	Reaction Model	
t	Specimen thickness	mm
w	Specimen Width	mm
E'	Storage Modulus	MPa
Δ	Stroke or support displacement to the origin	mm
$K(T)$	Temperature dependent rate constant	
H_T	Total heat of the reaction	
R	Universal Gas Constant	$JK^{-1}mol^{-1}$
dy	Vertical distance between loading bars	mm

Motivation and objective

The use of epoxy resins as matrix for a carbon fiber reinforced composite is regarded as a big advancement in aviation history. However, due to the nature of the resin and its cure process, there is a time interval in which the material can be used for fabrication. Since these prepregs are being used in Hot Forming which uses a thermal cycle to aid the forming process, a co-cure process will occur, which can degrade the material and reduce mechanical and physical properties. Therefore, there is a need to assess the maximum out time applied to material for Hot Forming process in order to maintain the mechanical and physical requirements. Material with greater out time and Shelf life is more focused since it can represent material with less out time and shelf life if the requirements are met. Therefore if the material with greater out time and shelf life is within requirements, assumption is made that the material can be used in Hot Forming and will assure product quality.

The goal is set to find out if higher out time material is able to fulfill and meet the requirements as well as maintain some work-ability qualities after hot forming. This will help Embraer by saving some fresh new material and re-use some of their material stored for hot forming process.

Thesis arrangement

For better understanding and organization, the thesis is organized as:

1. Introduction - Where composite fundamental and trivial knowledge is exposed as well as its applications and curing process. It also covers the fabrication flow of the tested panels and a brief explanation of each workstation;
2. Development - In this chapter material requirement, testing and fabrication are scrutinized and explained as well some other details involving the development of the thesis;
3. Physical testing of prepreg material - This chapter contains the physical testing and conclusions of said experiments along with procedure and description of each test;
4. Mechanical testing of cured laminates - Follows the same logic as chapter 3, but with mechanical testing and more detailed procedure and preparation;

1.1 Embraer S.A.

Embraer S.A. is an airplane manufacturer which excels at Regional Jets and Private Jets. Founded in 1969 with the support of the Brazilian government, it has manufacturing and assembly sites across the world, having a big international presence. In the late 70's the development of products such as EMB 312 Tucano and EMB 120 Brasilia allowed to a new step towards a new technological and industrial baseline [1]. After its privatization in 1994, it took 3 years to get into regional commercial aviation with the ERJ 145 family and later in 2004 with the E170/190 family jets. The development of the ERJ145 was delayed due to the financial crisis sustained during the early 90's. Its later expansion to executive aviation with the Phenom series and Lineage ,later with Legacy 500 series showed the world the ability to innovate and adapt.

Figure 1.1: The aircrafts of Embraer S.A., from top to bottom: Executive jets (Phenom 100, Phenom 300, Legady 450, Legacy 500, Legacy 600, Legacy 650 and Lineage 1000), EJets family (E195E2, E190, E175E2, E145XR, E140 and E135) and (E195, E190E2, E175, E170 and E130) and Defense and Security (KC390, Embraer 145 AEW and C, Embraer 145 Multi Intel, Embraer 145 MP, Super Tucano, and Ipanema) adapted from [2]

1.1.1 Embraer Portugal S.A.

In Évora, Portugal, Embraer has 2 sites: Estruturas em Compósitos S.A. (Composites manufacturing) and Estruturas em Metálicos S.A. (Metal manufacturing). Both these plants were announced by Embraer in 2008, and since 2012 Embraer Portugal S.A. has been active and working. In the composites plant, the main projects are the Legacy program, Phenom program, KC390 and ERJ-E2 programs. This plant follows lean manufacturing strategy and thus has a direct, counter-clockwise flow which can assure lean strategy between 3 main areas: Logistics, Fabrication and Assembly. It also has been recognized by European Agency Leed a silver grade lean strategy plant.

1.2 Composites: an approach

Since the beginning of mankind, history has been separated into Ages, i.e. Stone Age, Bronze Age, Iron Age, etc. We are living in an Age which cannot be described by a single material. Mankind has been using more and more resources, which have a lot of diversity and can now mix different resources and call them "composites". Make tiny little structures and call them "nanostructures". Use carbon based materials and make them the strongest materials to existence. There is not a main field of resources which can be use to describe this Age we are living in.

Nonetheless, composite materials have been developed greatly the last two centuries. Even though that concrete, for example, has been used since the Egyptians Pyramids, therefore being the one of the oldest materials used in our history. Nowadays, it is expected for composites to be the most type of material used in the world, due to the fact of its outstanding properties, achieving great strength with less weight when comparing to other kind of materials. Composites, by definition, are an heterogeneous mix between two or more main components: the matrix and the reinforcements. The matrix is the material that mantles the reinforcements and reinforcements is what is added in order to improve properties. Right now, composites have the advantage to produce what has not been able to produce with single materials matrix.

Due to its range of properties, it is expected an incredible range of uses. Covering most of the modern day industry applications such as aeronautics, automotive, sports and construction. It ranges from the most used material in the world, concrete, to optimized carbon fiber laminates. Composites are categorized in three major groups: **M**etalic **M**atrix **C**omposites, **P**olymer **M**atrix **C**omposites and **C**eramic **M**atrix **C**omposites. Then these have 3 subcategories: Particle-reinforced, fiber-reinforced and structural (figure 1.2).

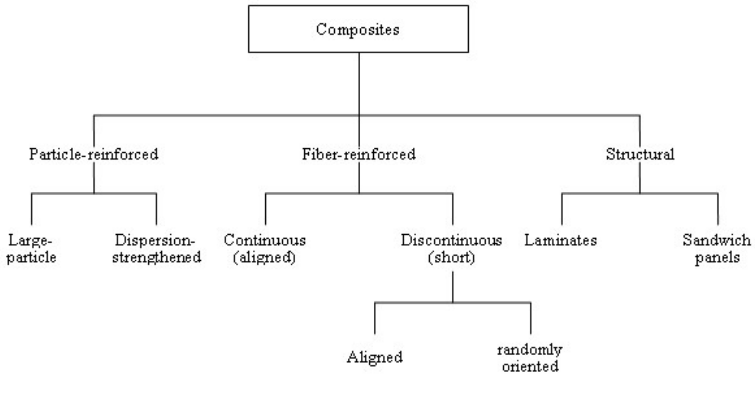


Figure 1.2: Reinforcement grouping from *Materials selection* [3].

Depending on application, each group of composite material is praised to be the solution. In aeronautics, the carbon fiber laminates are one of the most used composite materials, due to their strength to weight ratio and low thermal expansion coefficient[4]. Nevertheless, along with some other composite classes, the main failure mode is the interface between the fibers and the matrix. This is a major concern since this deficiency is highly damaging for the material if measures are not applied. As such, there is a great need to evaluate and measure the composite interface failures with mechanical tests as these will provide the most genuine failure compared to the real world. These tests will be described in section 2.2.3 and chapter 4. Most concepts and terminology used in aeronautics and this particular thesis are defined at ASTM D3878 [5].

1.2.1 Carbon Fiber Reinforced Polymers

Carbon Fiber Reinforced Polymers (CFRP) demand research to find out the right material mixture, since the ratio between resin and fiber is highly regarded in the final properties of the laminate. In addition, the process used is a big factor as well. Impregnating the resin whilst doing hand lay-up is not really the best solution. It will not create homogeneity and provoke resin accumulations. This will put the physical integrity of the resin/carbon fiber bond. Because of this, suppliers arranged a new set of material, preimpregnated carbon fiber, or simply, prepregs. This material comes with the carbon fiber embed with resin, so that the client does not need to worry about the mixing of this two products. The mix is already made to guarantee perfect fiber/epoxy matrix and ensures little to no variation. Prepregs come in various shapes and forms, but there are three main groups of carbon fiber prepregs: tape, tows or fabric. These products usually come in B stage (detailed at 1.3.2), one of the curing stages, to ensure better handling [6].

Thermoset and thermoplastic matrix are used in prepregs, although it is far more common to use thermoset resin, for example epoxy, polyester and vinyl ester. The main disadvantage of using a thermoset matrix is that it cannot be reprocessed. In the specific case of thermoset resins, after curing, the material cannot undergo another molding process. After resin components mixture, cure process starts to develop from room temperature. Slowing down the cure process is achieved by reducing the temperature (more information on section 1.3.2). This room temperature condition restricts the amount of hours the material has on room temperature, in terms of molding and layup processing, until it reaches a state of no processability. This defines and highlights the definition of out time and shelf life. It becomes a necessity to control out time to assure perfect material processability [7].

1.2.1.1 Resin

Thermoset resins, unlike thermoplastic resins, are defined by having a cure reaction. Thermosets are used over thermoplastics as result of its wide range of properties without changing any structure, by altering the amount of crosslinks in thermoset network. Since 90% of thermoset resins used are polyester resins, as consequence of being cheap to make, it would be expected for them to be used as matrix in prepregs. Still, the resins with better mechanical and high temperature performance are used. Epoxy resins are the next most important class of resins and there are no alike in all thermoset resin classes[8]. This is justified by:

1. Low volume reduction after cure, thus less residual stress inducted by resin shrinkage in laminate, than most thermosets;
2. Possibility of a wide range of temperature, by choosing thoughtfully the curing

agents to enable a good degree of crosslinking control;

3. Less applied pressure needed for fabrication of products, compared to other thermoset resins;
4. Possibility of having a range from low viscous liquid to tack-free solid.

Because of this, epoxy resins are used in a wide variety of applications, including adhesives, coatings, composites, but when needed, higher functionality epoxy are used in aerospace and critical defense applications [8]. Regarding versatility, epoxy resins can cure using an array of materials, with various types of curing conditions. Epoxy resin is chemically described as a low molecular weight organic liquid containing epoxide groups, illustrated in figure 1.3, which are three member rings of two carbon atoms and an oxygen atom. Cure reactions and more details at section 1.3.2.

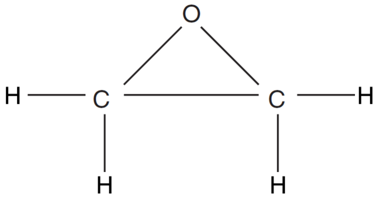


Figure 1.3: Illustration of a three member ring epoxy group, adapted from [8].

1.2.2 Composite Laminates

In this thesis subject, laminates are continuos carbon fiber reinforced epoxy resin which are laminated through hand layup or automated layup (more details on A.1.2). The carbon fiber continuos reinforcement will provide strength in the orientation of said fibers. Nonetheless, in the perpendicular direction, 90°, load is absorbed by the matrix, so, strength is characterized by the matrix, which is notoriously weaker. Hence, it is logical to design a laminate containing fibers oriented in multiple directions. Campbell [4] defines a quasi-isotropic laminate as a balanced laminate with equal number of plies in the 0°, +45°, -45° and 90°, or others. This proposal is highly regarded as optimal, since it provides laminates with great strength in multiple orientations.

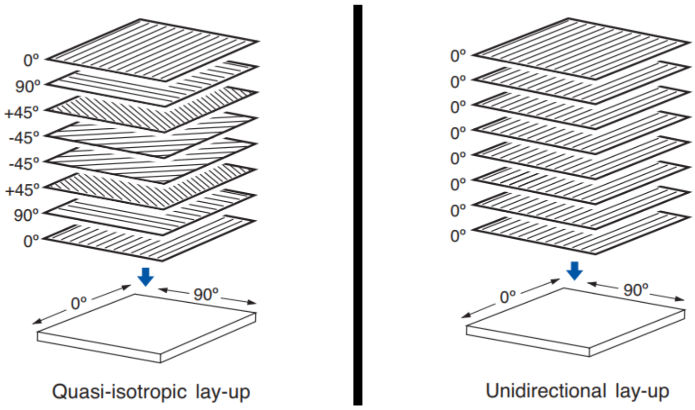


Figure 1.4: Orientations in a laminate and an example of a quasi-isotropic laminate adapted from [9].

Mechanical properties can be considered as a specific job appointed either to the matrix or the reinforcement. Longitudinal strength and compression loads are appointed to fibers whereas the matrix disperse the load between the fibers and prevents them from deforming under compression. A summary is provided in table 1.1. [4]

Table 1.1: Summary of dominating composite constituent on each mechanical properties, adapted from [4].

	Mechanical Property	Dominating Composite Constituent
Unidirectional	0° Tension	Fiber
	0° Compression	Fiber
	Shear	Fiber and Matrix
	90° Tension	Matrix
Laminate	Tension	Fiber
	Compression	Fiber and Matrix
	In-Plane Shear	Fiber
	Interlaminar Shear	Matrix

1.3 Fabrication

In Embraer, a flow of processes leads to grouping of processes. For example, fabrication is the group with all additive manufacturing technology to elaborate composite laminates and all the steps in-between. This section is detailed in appendix A.

1.3.1 Hot forming process

Hot forming is a mechanical process which forms the material to a mold using both temperature and pressure as ancillary forces. While temperature is achieved with heating lamps, pressure is achieved with vacuum pumps. The hot forming cycle has 6 steps:

1. Heating ramp;
2. Temperature stabilizing;
3. Vacuum starting ramp;
4. Hot forming baseline - Maximum temperature and pressure;
5. End of vacuum;
6. Cooling ramp.

While having a cycle similar to curing cycle, the temperature and pressure are lower. While temperature is assigned to be within room temperature and cure reaction temperature, pressure is near the pressure used in Autoclave during cure cycle. However, the pressure in autoclave process is enforced through the atmosphere (addition of H_2) while in hot forming a silicon membrane is used with vacuum to achieve the vacuum set point. The heating ramp, laminate thickness, system pre-heat and cooling ramp are definite factors to temperature uniformity. While this process is highly useful, due to the capacity to manufacture tight angles without porosity, the heat cycle deals a great maleficent to the prepreg resin. This reduces prepreg properties and may damage the prepreg to the point of no return. Being the main objective of this thesis, this work will look into the damage into prepreg resin and analyze it to assess its effects on aging material.

1.3.2 Cure

The epoxy resin cure is defined in three different stages [6]:

- A-stage: When both epoxy components, the base and the curing agent or hardener, are mixed but without any chemical reaction.
- B-stage: Intermediate state when chemical reaction has already started and material gets thickened and tacky. This stage is maintained when stored at -18 ºC.
- C-stage: Fully cured resin.

These stages are set to easily understand cure reaction and define curing phases in order to easily evaluate the curing degree of a material. As said before, cure reaction starts when both curing agent and base material are mixed. These curing agents, or hardeners, are picked regarding the applicable curing conditions and resin final application. The curing reaction is initiated with a reactive curing agent reacting with two epoxy rings where reticulation occur, in this specific case, with an amine curing agent. This reaction is exemplified in figure 1.5.

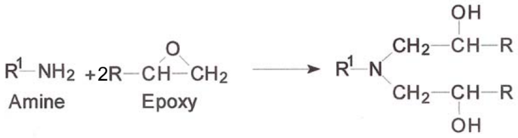


Figure 1.5: General cure process for epoxy resins using amine curing agent, adapted from [8]

The kinetics of this reaction are lead by temperature and time. To assess the relation between rate and degree of cure a lot of kinetic models have been developed over the years. Global reaction kinetic reactions are mostly used to characterize thermoset polymers (i.e. epoxy resin). Kinetic parameters of cure reaction can be found through DSC analysis. Adapting and citing Hardy Hardis [10], data gathered from DSC equipment can be fitted into kinetic reaction models. In appendix B final equation is achieved, equation 1.1, which endorses the key element that the degree of cure is directly correlated to temperature and time.

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(\frac{-E_A}{RT}\right)(1-\alpha)^n \tag{1.1}$$

With $\frac{d\alpha}{dt}$ as rate of cure, A as a pre-exponencial constant, β as heating rate, E_A as activation energy, R as the universal gas constant, T as temperature, α as degree of cure and n as constant of n^th order model.

However, for an homogeneous cure, activation energy must be provided to the resin for proper cure reaction, resin flow and proper cross-linking. Also, as expected, activation energy will be higher with the increased out time. This will directly affect the viscosity and risk the right temperature on which the viscosity on resin is optimal for volatile content to be withdraw from the resin.

1.4 Summary

Having composites as highly optimized materials regarding effectiveness, CFRP composites are highly valuable in aeronautics, aerospacial and automotive industry. While having a great weight-to-strength ratio, processability and process costs are relatively high. Also, it needs a highly specialized workforce and machinery. While focusing on CFRP prepreg composites there is the main issue of the time interval which the material can or can not be used due to the fact that the at room temperature the material is curing slowly.

For better understanding, the curing kinetics and resin are focused. Cure is defined by temperature and time, through an Arrhenius equation, meaning that both will affect and influence the cure reaction. Temperature affects the cure by providing the energy to crosslink the epoxy polymeric chains, and the longer the material is exposed above -18ºC, further is the degree of cure.

2.1 Summary

All requirements are defined by Embraer standards and the analysis made in this thesis is supported by those documents. However, most analysis are not related to Embraer's material standards since it is mostly a correlative study between the varying exposure conditions and the effect of hot forming thermal cycle in material mechanical and physical properties.

Nevertheless, Embraer's minimal mechanical requirements are going to be enforced and commented. The focus of testing will evaluate the conservation of material physical and mechanical integrity throughout exposure conditions and hot forming thermal cycle. As so, the following tests, testing conditions and exposure conditions are proposed to assess material solidity. Also, there are two material regarded for testing, divided by the two automated layup processes used to fabricate the samples: Automated Tape Layup (ATL) and Automated Fiber Placement (AFP) (more information on section A.1.2 of appendix A).

2.2 Testing

2.2.1 Testing conditions

Test condition will be at Room Temperature and Ambient conditioning (RTA), described below. Other testing conditions are advised, such as wet conditions as stated in ASTM D618 as ETW, but due to time constraints it was not possible to arrange such testing conditions.

- **RTA** - Temperature at 23 ± 3 ºC, with specimens conditioned in Ambient conditioning as ASTM D618/procedure A:
  - Condition 40/23/50 for specimens 7 mm or under in thickness - condition test specimens 7 mm or under in thickness in the standard laboratory atmosphere for a minimum of 40 hours immediately prior to testing. Provide adequate air circulation on all sides of the test.

2.2.2 Physical testing

Due to the nature of the prepreg, most physical testing will focus on uncured prepreg. These tests will help us assess the material properties before and after the co-cure provided by hot forming thermal cycle. Each one of this physical tests are intended to a specific function, according its results and functioning. However, ply thickness is measured in cured laminates. Although it is not a prepreg test, it is a measure of a physical property, therefore will be considered a physical test.

- Ply thickness;
- Fourier Transform Infrared (FTIR);
- Differential Scanning Calorimetry (DSC);
- Dynamic Mechanical Analysis (DMA).

2.2.3 Mechanical testing

Mechanical testing is needed to aid the scope of this thesis to properly evaluate the prepreg after hot drape thermal cycle and exposure conditions. It will be important to assess the effects of the thermal cycle, together with material exposure.

- Interlaminar Shear Strength (ILSS).
- Interlaminar Tension Strength (ILTS)

2.3 Material exposure conditions

The material exposure conditions are expressed in table 2.1. In order to optimize production, conditions 1 to 4 will be laminated in bulk, except for the 'L' shaped mold. Condition 5 requires a more complicated aging, with revalidation tests to assure material quality.

Table 2.1: Material exposure conditions

Condition	Material Out Time	Hot Drape	Additional Out Time After Hot Drape	Cure
1	Minimum [1]	No	No	After lamination
2	Minimum [1]	Yes	No	After hot drape
3	Maximum [2]	Yes	No	After hot drape
4	10 days for ATL material 11 days for AFP material	Yes	Maximum [2]	Out time limit
5	Revalidated +200h	Yes	No	After hot drape

[1] 2 days of accumulated out time allowed

[2] 14 days for ATL material and 15 days for AFP material of available out time allowed

2.4 Fabrication

While sorting material to use for experimentation, shelf life was highly regarded. Out time had a special importance in selecting tows for AFP, since there was a high volume of material within our exposure conditions. Hence aging was mostly for condition 5, regarding AFP material. After material selection, material would unfreeze for 8 hours at least. In some cases, different batches were used in producing the same panel. Out time condition was regarded higher than batch uniformity, since this would save material that could be used for Embraer production. For ATL, material started from scratch, using a fresh spool of material. After laminating, the panels went through an aging process to allow exposure conditions to be met.

Vacuum bagging led to some discussion and troubleshooting, since at first, non-porous Armalon was used underneath and over the laminate, followed by a breather/bleeder fabric and plastic vacuum bagging film. When releasing the laminate from the mold, all release film, which was applied before, was absorbed by the non-porous armalon. This attached the laminate to the mold and demolding was inappropriate and burdensome, causing the laminate to present some fractures. After that, looking at previous specimen fabrication and Hexcel recommendation [9], vacuum bagging was assembled as follows:

Furthermore, mold was not completely solid and had gaps along the 'L' shape. This made the autoclave process to push the laminate into those gaps, since it was projected to have excess. This lead to two panels from ILTS condition 1 to be partially fractured

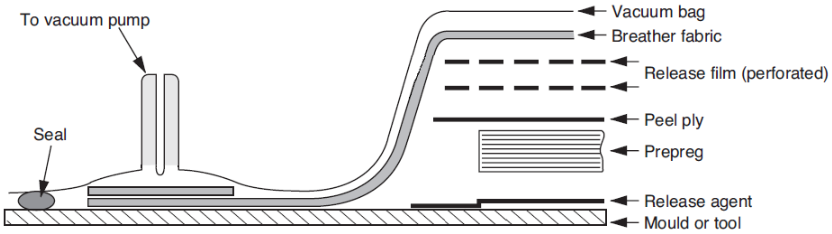


Figure 2.1: Representative vacuum bagging on panel fabrication adapted from [9].

as well, in order to be demolded. Also, there were some resin leaks into those gaps and cured beneath the ’L’ shape. This may have lead to a decrease of performance from the laminates, although not really as much as thought, since the laminate has enough thickness to withstand such resin leakage.

As previously mentioned, all the panels were laminated using either ATL or AFP, both using CNC programming. Therefore, lamination programs had to be developed, with help from Embraer engineers. Torlay (ATL) and Ingersoll (AFP) software was used to achieve the final lamination programs. These programs are designed to laminate the tapes/tows necessary to fulfill the product line and the excess line, as well as gap control, stagger and repetition patterns. All laminates were laminated in the 0º direction. The ILTS laminate was manufactured with too much excess for the mold size (since the excess was pushed into the gaps of the mold as explained before), although it was rather useful for extract enough material for physical testing. ILTS laminates also had some complications with the condition 1, since both condition 1 laminates were laminated by hand layup of sets of 6-ply laminates and molded into the ’L’ shape with the help of vacuum. This lead to some porosity and wrinkles in the radius area, as well as the reduction of sample size on both condition 1 ILTS panels.

2.4.1 Panels and specimens

Panel fabrication was planned regarding the tests needed and which requirements were needed to meet. Considering the fact that two mechanical tests were intended, two panels were to be manufactured. One regarding ILSS test, which were used to DMA as well, and one regarding ILTS. As both have to fulfill material exposure conditions detailed in section 2.1, a panel would needed to be manufactured for each condition. Therefore, a total of 20 panels were created.

For each panel, intended sample size was of 10+ specimen. However, because of some constraints regarding panel quality mentioned in section 2.4, some panels sample size were reduced.

Chapter 3

Physical testing of prepreg material

3.1 Ply thickness

Ply thickness will be measured using 10 random points in the laminate after curing and before specimen cutting. It will allow us to determine if the laminate is consistent in its full extent, as well as determine if there is defects in the laminate. If data scatter increases significantly after normalizing, the reason must be investigated.

The 10 thickness measurements in each group of panels with the same number of plies and utilizing the formulation presented below. The same procedure ought to be done to test specimens as well, however performing 3 measurements instead of 10. The nominal ply thickness is calculates using the following expression:

$$T_p = \left(\frac{\frac{t_1}{N_p} + \frac{t_2}{N_p} + \frac{t_3}{N_p} + \ldots + \frac{t_i}{N_p}}{n_m} \right) \tag{3.1}$$

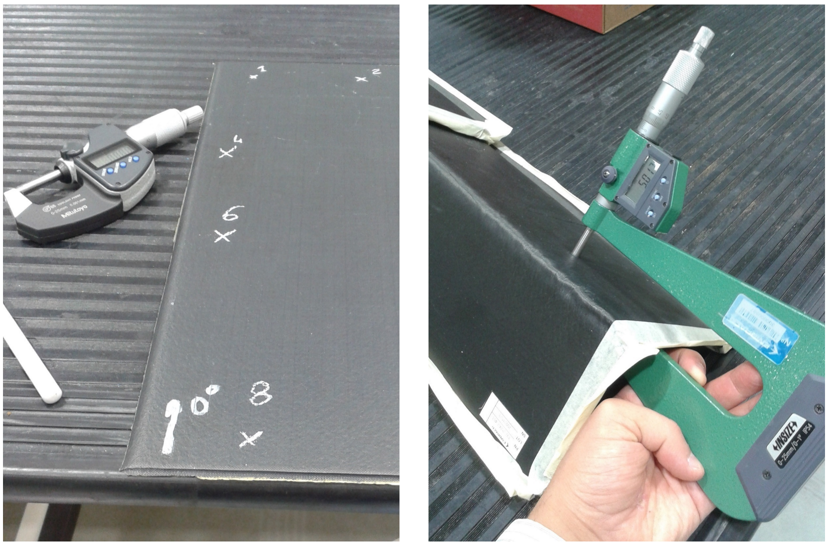
Where T_p is nominal ply thickness, N_p is number of plies, t_i is the thickness of panel "i"and n_m is the number of measurements. In accordance with equation 3.2, the average nominal thickness from the panels is used to obtain the nominal thickness:

$$T_n = \frac{\sum T_{pi}}{n_p} \tag{3.2}$$

Where T_n is normalized ply thickness, n_p is the number of panels and T_{pi} normalized ply thickness of the "i"panel.

3.1.1 Procedure

To accurately measure the laminate, a micrometer is advised. However, in some cases, to accurately measure a more complex laminate, a specific micrometer was used, as shown in figure 3.1:



(a) Regular micrometer measuring (b) Larger micrometer measuring

Figure 3.1: Micrometer measuring for calculating Normalized Ply Thickness.

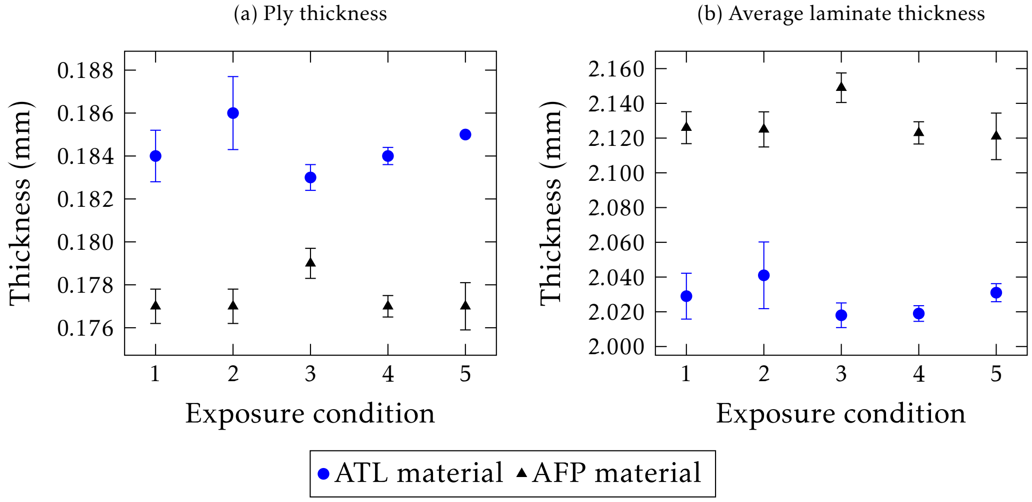
3.1.2 Results and discussion

Using equations 3.1 and 3.2, a brief summary is present in table 3.1:

Table 3.1: Ply thickness and average laminate thickness in paranthesis, expressed in millimeters (mm)

Process	Condition 1	Condição 2	Condition 3	Condition 4	Condition 5
ATL	0,184 (2,029)	0,186 (2,041)	0,183 (2,018)	0,184 (2,019)	0,185 (2,031)
AFP	0,177 (2,126)	0,177 (2,125)	0,179 (2,149)	0,177 (2,123)	0,177 (2,121)

In a first instance all results are according to expected, and specifically ATL material is basically spotless. However, at a second analysis, ply thickness from AFP material is too thin. This may be related with vacuum bagging, since perforated release film was preferred, leading the resin into the breather fabric. Therefore, the usage of non-perforated release film would be preferential. That would allow the resin for consolidate better and create a better interface between matrix and reinforcements. Notwithstanding, ILSS mechanical test will allow to corroborate that this thickness difference will not be as influential as predicted in section 4.1.


(a) Ply thickness

(b) Average laminate thickness

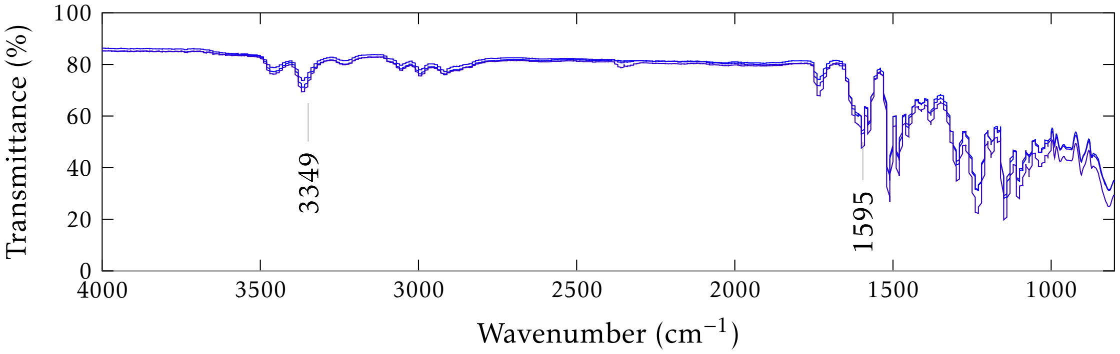
Figure 3.2: Ply and thickness depicted with exposure condition and process.

3.2 Fourier Transform Infrared

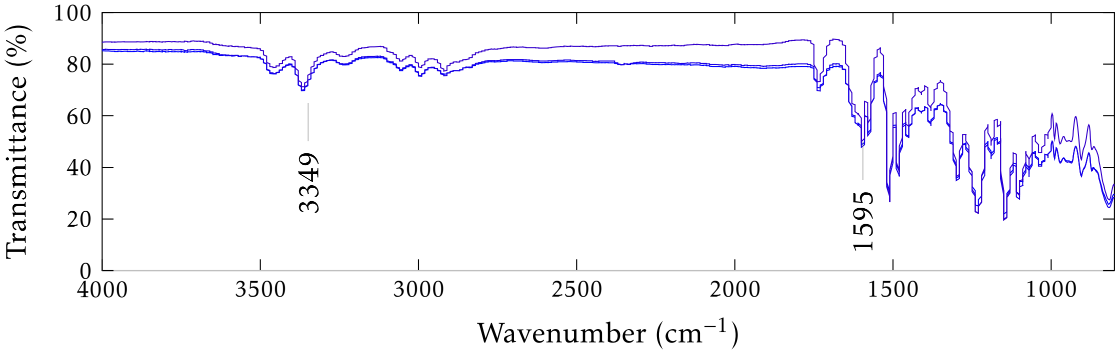
FTIR it will be used to evaluate the material in a whole, regarding the eventual inclusions and impurities present in the material. This will help us define if there is more in the prepreg than necessary for product quality, specially after hot drape. Although there are measure to prevent it, there may be some exchange of material between the prepreg and the hot drape screen.

3.2.1 Procedure

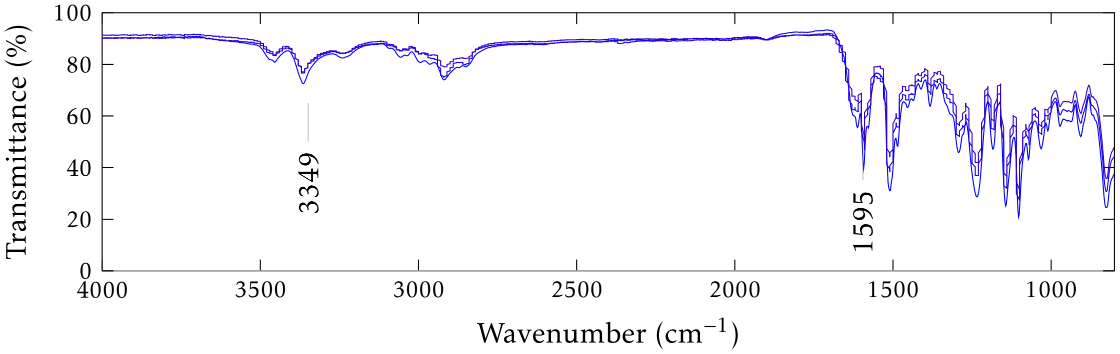
This test was made with ATR support, which allowed us to test the prepreg directly without sample preparation. Samples were pressed with a tip using a swivel pressure tower, which allowed the sample to be directly in contact with the crystal below the



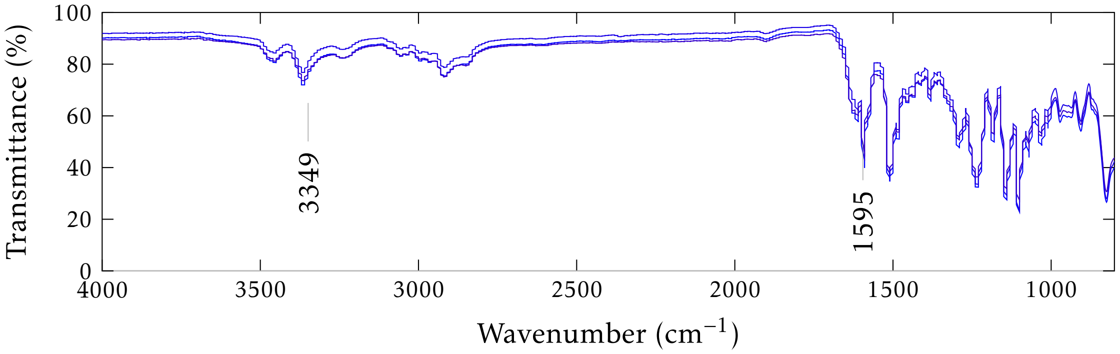
(a) ATL material without hot forming process.



(b) ATL material with hot forming process.



(c) AFP material without hot forming process.



(d) AFP material with hot forming process.

Figure 3.3: FTIR results using ATR of before and after hot forming process for ATL and AFP materials, 3 samples corresponding to condition 1, condition 3 and condition 5.

pointer. Considering that the crystal is between the emitter and receiver of the machine, the contact with this crystal will ensure sample testing.

3.2.2 Results and discussion

As this test was a method to identify any chemical bonding change in the prepreg before and after hot forming process, the analysis process regarding the results will be simply determine two of the most crucial peaks to prepreg material, 3349 cm^{-1}, related to typical vibrational mode from hydroxyl group, and 1595 cm^{-1}, related to typical vibrational mode from the bonding between two aromatic groups (C-C) [11], linked to the curing agent. The rest of FTIR graph analysis will be to determine if there is any significant differences between the material before and after hot forming process.

After close analysis of the graphs, there is no evidence of any chemical inclusion from hot forming process, as there is no odd peaks between the two set of samples. There is a small difference in some samples of transmittance, justified with machine error or baseline miscalculation by the software used to obtain these results. Still, it is not a decisive factor to affect inclusion analysis.

3.3 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a thermoanalytical test to which measures the heat necessary for molecular transitions in the material to happen. In this particular thesis, DSC is going to be used to study and measure the glass transition temperature, or T_g, of the prepreg resin, in order to assess the purity of it as well as to guarantee its required physical properties. Quoting Höhne *et al.* [12], DSC means the measurement of the change of the difference in heat flow rate to the sample and a reference sample while they are subjected to a controlled temperature program.

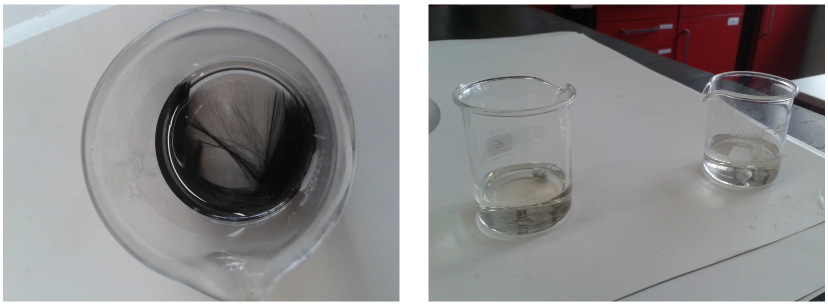
3.3.1 Procedure

For DSC, intended sample is neat resin. Therefore, resin had to be withdrawn from the uncured CFRP. For this, using a dichloromethane (DMC) solvent to easily extract the resin from the uncured composite.

First, in a fume hood, a sample of prepreg is soaked in DMC and the fibers should be manipulated to obtain the most neat resin as possible, as in figure 3.4(a). After fibers removal, we have a solution containing the resin and the solvent, figure 3.4(b). To extricate the resin, the solution must be heated to 40 ºC to evaporate the solvent, figure 3.4(c). This should be aided with a magnetic mixer in order to avoid heating heterogeneity.

Then, the obtained resin should be measured and sealed inside a container. The sample should weight around 7 to 10 mg, although it is acceptable to use sample weight to 15 mg, figure 3.4(d). After measurement, it is wise to seal the container store it in -18 ºC to avoid resin degradation.

When it is time to test the samples, material should be taken at least 8 hours before testing, to properly assure that the material is not frozen or with residual humidity. Heating rate was 10ºC/min and the range was between room temperature to 300ºC.



(a) Fiber manipulation in DMC.

(b) Beaker with DMC plus resin mixture ready for solvent evaporation.

(c) Solvent evaporation with the assist of a heat plate and magnetic mixer.

(d) Sample measurement assisted with a scale.

Figure 3.4: Illustration of DSC specimen preparation.

3.3.2 Results and discussion

As mentioned before, DSC will provide us with the glass transition temperature, T_g. As Alis and Sasaki [13] states, there might be a relation between T_g and mechanical properties. Also, T_g it is expected for T_g to increase with prepreg ageing, according to Ahn *et al.* [14] and Frigione and Kenny [15]. Since this test was time consuming, sample size was reduced to two samples for either ATL and AFP material. One from exposure condition 1 and another from exposure condition 5. This would allow us to evaluate the effects of ageing in T_g. Also, DSC also provides two other sets of data which are useful to understand the effect of exposure condition on the prepregs. First is the heat of reaction, calculated from the area of the complex peak in DSC results. In addition, the heat capacity of the prepreg at the glass transition temperature will also be considered analysing the prepregs. Detailed information is not shown due to confidentiality terms.

As expected, T_g increased over exposure condition, which supports the results obtained by Ahn *et al.* [14] and Frigione and Kenny [15]. This is due to the movement constraint of the material when curing process reticulates the epoxy resin, leading to an increasing T_g.

However, as foreseen by Odegard and Bandyopadhyay [16], heat of reaction decreased with exposure and heat capacity increased. This event is connected with a phenomena called Enthalpy relaxation, which is directly connected with annealing in the work of Lin *et al.* [17], however, in equation 1.1, it is concluded that the degree of cure is dependant

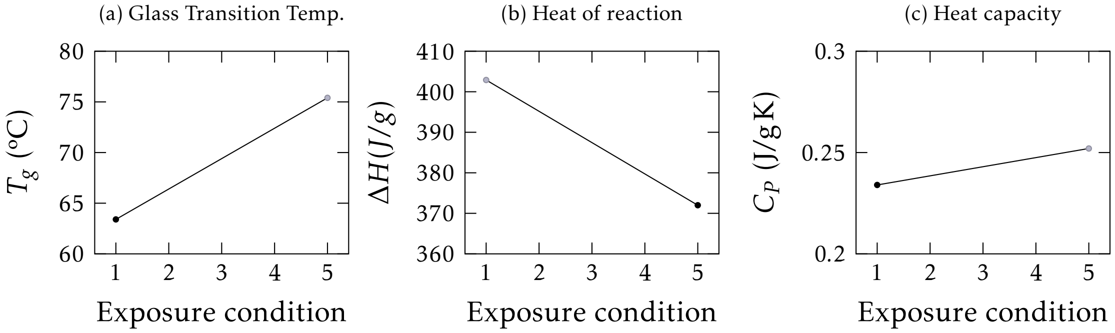


Figure 3.5: DSC data for ATL material.

on temperature (hence the annealing studies) and time (hence ageing studies).

Therefore there is a logical connection between the both, validating the theory that enthalpy relaxation is the cause of this results and this material thermal degradation in general.

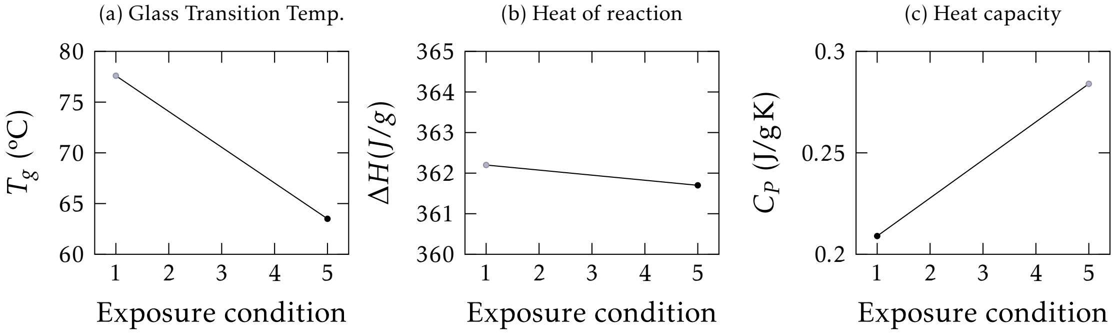


Figure 3.6: DSC data for AFP material.

Unexpectedly and differently from ATL material, T_g decreased over increasing material exposure condition. This is probably due to some error in the T_g measurement, machine data collecting or sample mass measurement. The latter is the most likely since the mass measured was so low, around 15 mg, which enables the minimal mistake to add or subtract a high percentage of the final mass. Also, the fact that only one sample is regarded for trending is not ideal for this analysis. Heat of reaction and heat capacity nonetheless are a bit off that what's expected, after analysis of this material mechanical response to exposure conditions, in section 4.1. Notwithstanding, this results are indeed according to literature on the subject, on which the material thermal deterioration with exposure is due to the enthalpy relaxation.

This phenomena, according Haque *et al.* [18], produces changes in physical and mechanical properties of a material, while are often observed in the region of the glass transition temperature during heating. As a material becomes more amorphous it becomes thermodynamically more unstable, leading to a decrease over time of enthalpy and specific volume, due to the relaxation of molecular structures toward their equilibrium state.

This means that when the material is deprecated, using time or temperature, it creates separated nucleus of semicrystallined epoxy rings, making the general material to be more heterogeneous. When the cure process is applied, material do not crystallize properly due to increased free volume and therefore weakening the thermal properties of the material.

3.4 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) is a analysis tool which can provide either thermal and/or rheological information from a certain sample. It actually can be called either Dynamic Mechanical Analysis or Dynamic Mechanic Thermal Analysis, depending on the application or area of study it is used, according to Menard [19]. To easily describe this test, Menard [19] describes it as a oscillating force to a sample and analysing the material's response to said force. This allows to gather certain material characteristics as the resistance the material has to recover from the oscillating force (complex modulus). Complex modulus (E^*) is the combination of two different modulus, the storage modulus (E') and the loss modulus (E''). Also, delta Tan (or $\tan\delta$) and T_g are other properties that will be evaluated by DMA.

3.4.1 Procedure

This test was executed according to ASTM D7028 [20], with a frequency of 1HZ, heating rate of 5 ºC/min and 20% of constant strain. Since either FCT/NOVA or Embraer had the resources to do this test, a company was entrusted with Element Materials Technology in Seville, Spain. Detailed information is not shown due to confidentiality terms.

3.4.2 Results and discussion

DMA results analysis will be done considering the values at glass transition temperature, to every exposure condition from both ATL and AFP materials. The glass transition temperature is actually a vitrification, resulting from the cross-linking reaction of the cure prepreg [21]. According to Frigione and Kenny [15] and Yu *et al.* [22] and results in 3.3.2, it was expected an increasing T_g with an increasing exposure condition. However, in both ATL and AFP materials this observation is not visible in DMA results, figures 3.7 and 3.8. This is because as Yu *et al.* [22] mentions, some different T_g are distinct from each other due to phase separation, implying that the material presents as an heterogeneous solid, probably being caused by the ageing process.

Regarding the storage modulus, it was expected to increase the plateau before vitrification, which means an increase in E' before vitrification [22]. In ATL material a slight increase is visible, but in AFP material there are no notorious change, which can be attributed to the material's capability to withstand exposure conditions.

Furthermore, when analysing the E'' and $\tan\delta$ for ATL material, there is a general proneness for decreasing with exposure conditions [22], while analysing the same parameters for AFP material, there is no general tendency, values keep oscillating but in a confined interval. These values are highly related since $\tan\delta$ is actually defined in equation 3.3.

$$\tan\delta = \frac{E''}{E'} \tag{3.3}$$

Looking at how the two materials behaved in this test, it is clear that ATL material is not as resilient to exposure conditions comparing to AFP material, since the AFP material reveals the stabilized values of either E', E" and tan δ. This reveals that the material does not present the same kind of heterogeneity that the ATL material does, when exposure conditions are applied, providing the information that glass transition zone is not changed and its mechanical behaviour is not debilitated, opposing ATL material.

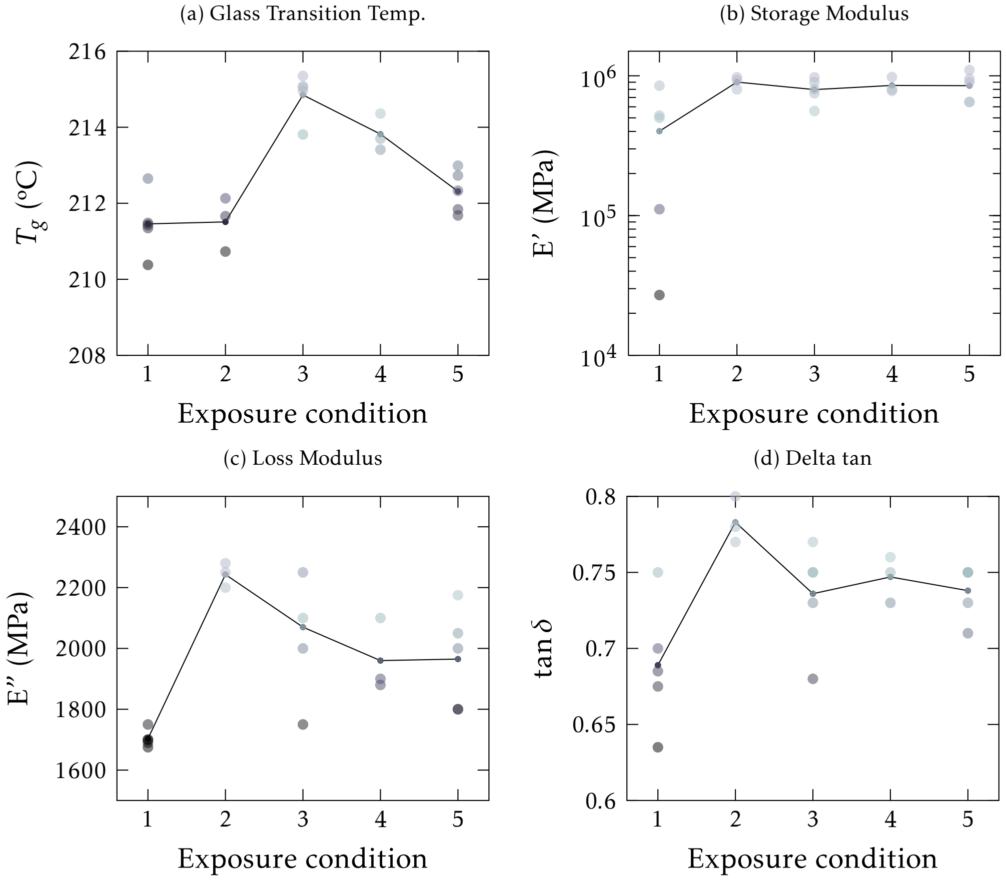
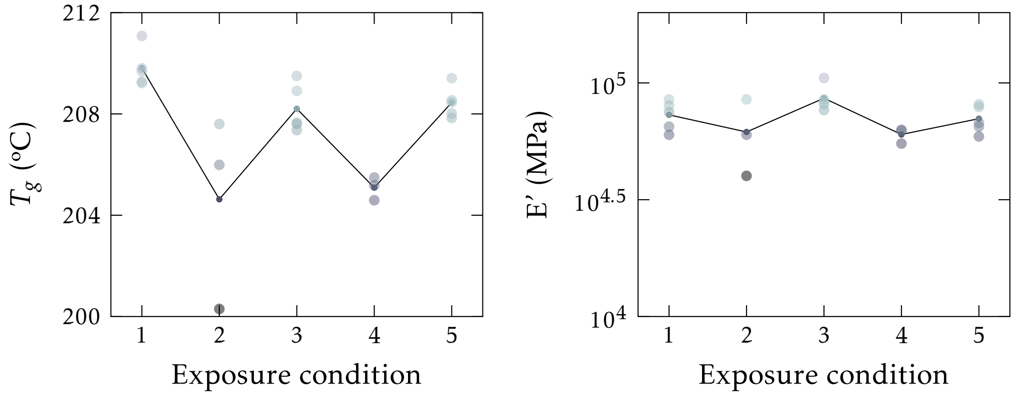
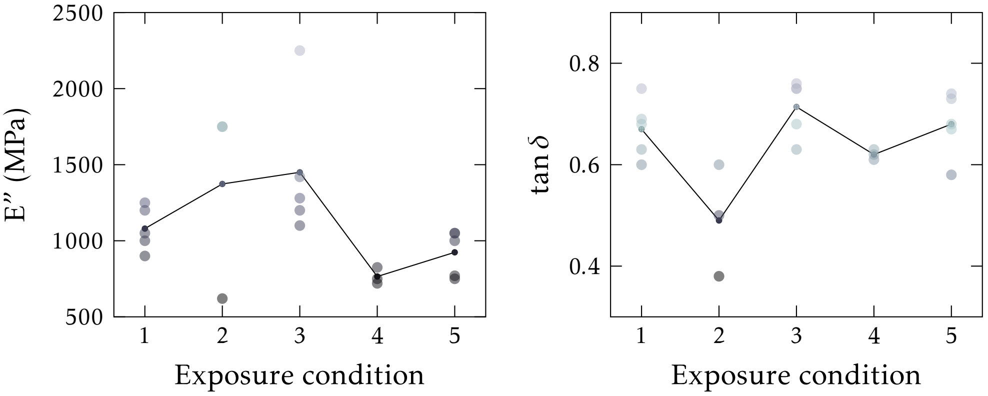


Figure 3.7: DMA data for ATL material.


(a) Glass Transition Temp.

(b) Storage Modulus


(c) Loss Modulus

(d) Delta tan

Figure 3.8: DMA data for AFP material.

4.1 Interlaminar Shear Strength

ILSS test was executed according EN2562 for ATL material [23] and ASTM D2344 for AFP material [24]. As so, specimen dimensions should be as follow for both ATL and AFP material, in table 4.1. ILSS is one of the most useful tests while testing laminates, since is relatively easy to execute, is quick, cheap (due to reduced specimen dimensions) and is representative of the process. Specimens are to be cut through CNC waterjet machine.

Table 4.1: Specimen dimensions for ILSS test

Material	Dimension (mm)	Thickness (nr. of plies)
ATL	20,0 ± 0,25 x 10,0 ± 0,2	11
AFP	$(6 * t^1 \pm 0{,}25)$ x $(2 * t^1 \pm 0{,}2)$	12

[1] Laminate thickness (mm)

Failure modes were otherwise similar to what is sketched in figure 4.1, as it is the normal failure mode of ILSS testing.

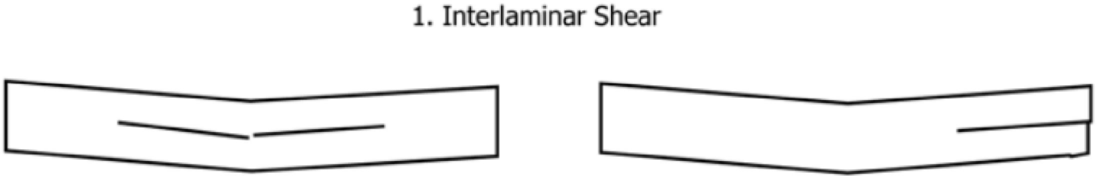


Figure 4.1: Failure mode for ILSS, from ASTM International [24].

This test is important because it is one of the tests that really assess the matrix and the interface matrix to reinforcements, compressing the laminate perpendicular to the direction of the reinforcements.

4.1.1 Specimen preparation

CNC waterjet cutting machine, detailed in A.1.3, is used to cut specimens and ensure the dimension and tolerance as well as a clean cut as exemplified in figure 4.2(a).

After cutting, specimens are identified from 1 to 15 and measured with a micrometer, as it is in figure 4.2(b). Tolerances in both standards had to be enforced, so that we could comply with said standards. Also, before testing specimens would be numbered and categorized by process (ATL or AFP) and exposure conditions.

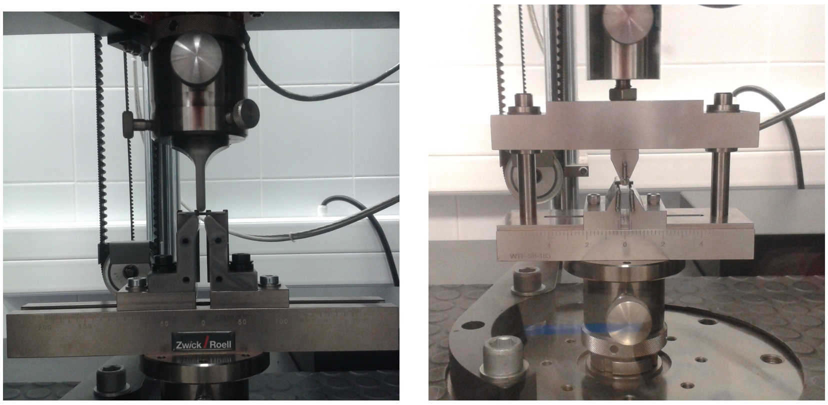
4.1.2 Test and machine preparation

Both material testing speed was 1 mm/min, although there was a difference in the lower support diameter for both materials. In ATL material an upper support with 6 mm diameter was used with a lower support with two 6 mm diameter supports, see figure 4.3(a), while with the AFP material an upper support with 6 mm was used with a lower support with two 3 mm supports, at figure 4.3(b).

(a) CNC Waterjet cutting of one panel for ILSS testing.

(b) Measurement and specimen identification.

Figure 4.2: Example of ILSS specimen preparation.



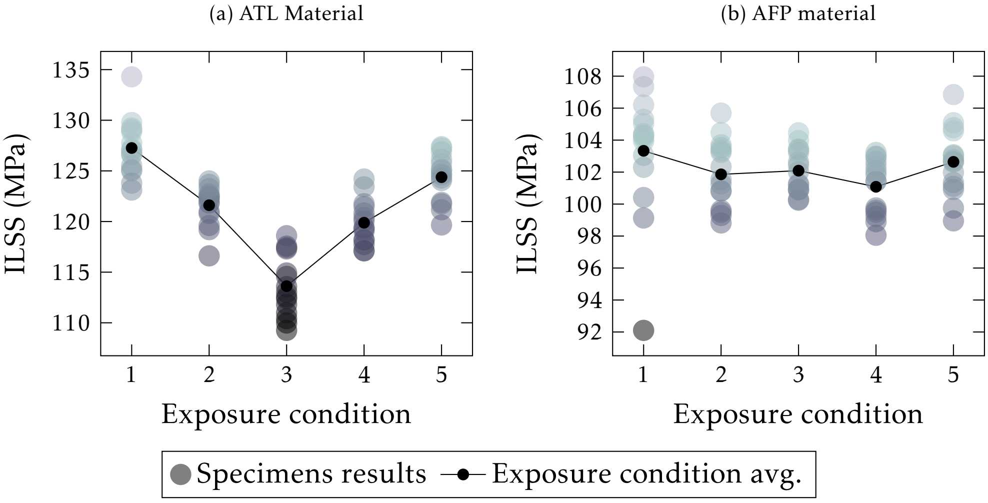
(a) ATL material testing setup with supports.

(b) AFP material testing setup with supports.

Figure 4.3: ILSS support and setup examples for both materials

4.1.3 Results and discussion

Summarized test results are illustrated on figure 4.4 while detailed information is not shown due to confidentiality terms.



(a) ATL Material

(b) AFP material

Figure 4.4: Interlaminar Shear Strength results from both ATL and AFP material.

In ATL material, it is noticed that there is a clear dip in the condition 3 of exposure conditions, which is the one that has the second most time of exposure. As such, there is a clear correlation between exposure time and material degradation, however, it is acceptable according to Embraer standards. Even so, there are some results which are challenging to embrace. For example, the condition 5 of ATL material clearly increases from condition 4. In fact, it is the condition with better results, even though it is the most aggressive condition in terms of material exposure. In fact it is the only outlier of this test. Despite that, ATL material results illustrated what is expected from this material, which is properties degradation over exposure time. This degradation over exposure time can be explained with the molecular heterogeneity and degree of cure, explained before in section 3.3, which reduced cross-link density that affected the adherence between lamina.

When looking at AFP results however, there is a distinct difference between ATL material, regarding properties over exposure time. This material apparently has a higher resistance to ageing, compared to ATL material. There is a small decrease over time in terms of the average results, but not significant enough to determine if exposure conditions were a big influence.

4.2 Interlaminar Tension Strength

Interlaminar Tension Strength shall be done according to ASTM D6415 [25], in which the specimens are stated for both ATL and AFP material, in figure 4.5. These specimens are going to be manufactured in a 'L' shaped mold, in order to provide the necessary angle and shape to the specimens for testing. Due to exposure condition number 1 (section 2.3), some hand lay-up was needed and developed using this method:

1. Using ATL or AFP, lay-up up to 6 plies in a flat surface;
2. Hand lay-up the 6-ply laminate into the mold surface and apply vacuum;
3. Repeat until all plies are laminated.

Since there was major restrictions about this test, specifically the support use, it was only possible to evaluate condition 1 from AFP material. However, the results will help to assess the how this material behaves when bending.

4.2.1 Specimen preparation

ILTS specimens were cut by disk cutter thanks to the imposed 90° angle, that makes it a near impossible task to cut by CNC waterjet machine. However, a test was conducted to assess disk cutter ability to cut specimen without damaging edges and generate delaminations. The arrangement was that specimens would be cut with disk cut aided with water as lubricant, since it was the only option which didn't delaminate the specimens.

4.2.2 Test and machine preparation

For this test, speed was set to 1 mm/min, although speeds up to 2,5 mm/min are acceptable, since the time that will be saved won't really harm final results. The supports used are from CENIMAT, but the testing machine did not allow for the test work in compression, therefore, the testing was done differently than represented in ASTM D6415.

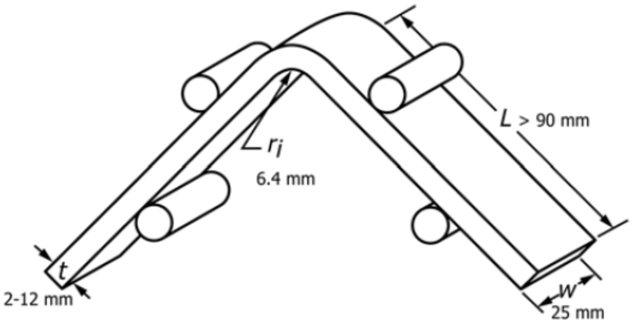


Figure 4.5: Dimensions for ILTS specimens ASTM International [25]

Test setup was done with upper supports with a distance of 53,8 mm and 10 mm diameter roller supports and lower supports with a distance of 104,4 mm with 10 mm diameter roller supports. The specimen would fit in between both supports and then compressed by traction forces as depicted in figure 4.6.

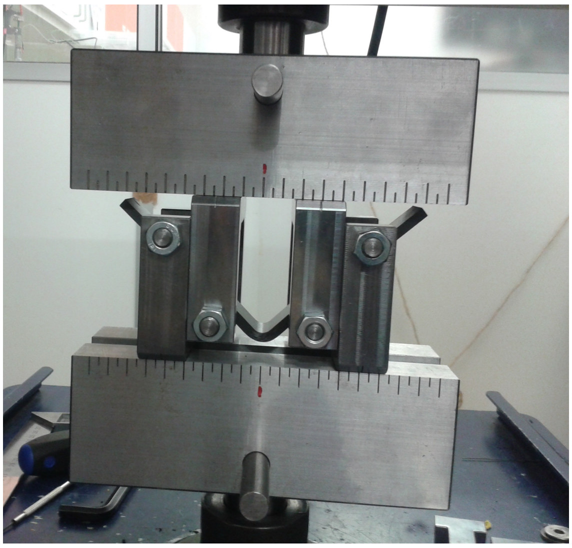


Figure 4.6: Representative case of ILTS setup used at CENIMAT's Universal Testing Machine.

4.2.3 Results and discussion

ILTS results were calculated using the following equations detailed in ASTM D6415, which had in account the change in test setup and support dimensions.

First, CBS (Curved Beam Strength) must be calculated, since it is the main mechanical property, by assessing the moment applied in the curved section of the specimen (figure 4.7 illustrating the scheme used to achieve these results):

$$CBS = \left(\frac{P}{2w.\cos\psi}\right)\left(\frac{dx}{\cos\psi} + (D+t).\tan\phi\right) \tag{4.1}$$

Since the displacement Δ, stroke, makes the specimen to open, the value of psi varies. To calculate this angle, it is necessary to first calculate the vertical distance dy.

$$d_y = d_x . \tan\psi_i + \frac{D+t}{\cos\psi_i} - \Delta \tag{4.2}$$

ψ_i is 45º, from the original 'L' shape specimen, which is half the original 90º angle formed by the specimen. Using trigonometric functions, ψ can be achieved using d_x and d_y:

$$\psi = \arcsin\left(\frac{-d_x.(D+t) + \sqrt{d_x^2 + d_y^2 - D^2 - 2.D.t - t^2}}{d_x^2 + d_y^2}\right) \tag{4.3}$$

After this equations, the ASTM D6415 presents an approximate simple calculation to calculate maximum ILTS:

$$ILTS = \frac{3.CBS}{2.t.\sqrt{r_i . r_o}} \tag{4.4}$$

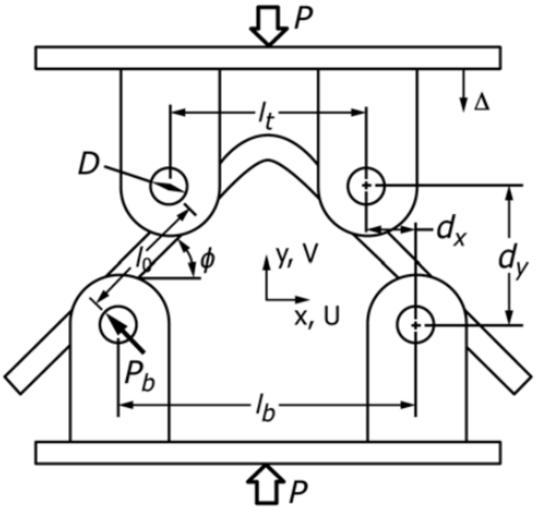


Figure 4.7: Schematic of ILTS setup from ASTM International [25].

Using equation 4.4, the following results were retrieved from 7 speciments:

Table 4.2: ILTS results from condition 1 of AFP material

Specimen nr.	ILTS (MPa)
1	92,85
2	87,74
3	58,37
4	71,36
5	89,91
6	87,27
7	76,66

With the following statistics, also calculated according ASTM D6415, it shows that the dispersion of specimen values is not huge, which allow to conclude that the specimen can be tested with this setup.

Table 4.3: ILTS results statistics from condition 1 of AFP material

Average ILTS (MPa)	Standart Deviation (MPa)	Coefficient of Variation (%)
80,59	12,43	15,42

Chapter 5

Conclusion and future work

Due to its range of properties and possibilities, composite materials are the next step towards technological improvement and sustainability. Furthermore, CFRPs are the future in aircraft manufacturing, mainly due to their strength to weight ratio, which allows aircraft mainframes to endure the forces required to takeoff, cruising and landing whilst also being light weighted.

As such, there is the need for enterprises like Embraer to adapt their processes to this technology. This thesis should respond to the main question of material supporting the exposure conditions. This will allow a better organization of storage material and optimize consumption.

First and foremost, there is a dispersion associated with human error, testing machine error, manufacturing processing, materials raw nature and laminates nature. These are errors which we cannot neglect, but in this thesis the dispersion was not affecting our results directly as much. Also, material degradation is not only due to the effect of material exposure, since degradation involves processability, which directly affects laminate quality, with low tack and/or drape.

As for DSC, revealed valuable information on how glass transition temperature increases with exposure conditions and how it will affect mechanical properties, via the enthalpy relaxation phenomena. There is also an apparent relation between heat of reaction and heat capacity with material deterioration. Notwithstanding, it is recommended for DSC testing to also study the activation energy (E_A. This should be done using various heating rates to calculate the correct model for cure kinetics [26]. DMA testing also provided information on how the storage modulus can increase and loss modulus decrease with aggressive exposure conditions. To evaluate better the material, a frequency sweep should be done as well, to achieve various glass transition temperature to study to calculate relaxation energy and activation energy [27]. Concerning FTIR testing, there was no evidence of chemical inclusion on the prepreg either before or after hot forming processing.

Mechanical testing revealed a weakened ATL material towards harder exposure conditions, while AFP material did not have severe variations on its results of Interlaminar Sheer Stress. In matter of Interlaminar Tension Strength testing, it is a test method recommended for future development of this topic. Being more complete than ILSS, it provides information about how the material behaves while bending, compression and how it will delaminate. This information can be used to assess the validity of a material for hot forming use, since the 'L' shape with 90° degree angle is one of the most common for hot forming, seeing that most product developed in hot forming process is spars or spar related product.

The work developed in this thesis should clear out that ATL material is not suited for exposure conditions while AFP material is capable of tolerate the exposure conditions proposed and be processed through hot forming. In most tests, ATL material clearly confirmed the theories supporting the variation of physical and mechanical properties while AFP material did not clearly verified those same variations, on which this work can conclude that AFP material is developed to resist to exposure conditions.

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A.1 Fabrication

Fabrication is where parts are manufactured. It follows a workflow designed to be fast and accessible. That flow follows the same organization as the following sections:

- Freezer and Cutting room
- Layup process
- Cure process
- Quality assurance

Each workstation has a specific purpose and serves as a main facilitator to achieve product quality. As factory layout follows lean strategy, paths and movement are optimized, reduced and close to each workstation. Hot forming and cure process already are defined in section 1.3

A.1.1 Freezer

When a material is received, it has to be stored in a special environment to minimize the cure process at room temperature. Suppliers tend to suggest a temperature to store the material, usually around -18ºC. This allows the storage and usage of the material when necessary, without worrying about the integrity of the material. The lean strategy used is First In First Out, where the oldest batch is the first at being used in production, while preserving the newest batch.

Using a specific stock management software, material out time is controlled, as well the quantity of material used in each production. Control over exposure temperature is highly recommended by suppliers to ensure B stage is maintained and to keep room temperature curing from occurring.

A.1.2 Layup Process

As one of the most used process in composites world, layup process consists in the stack of plies in a specific sequence and orientation where either hand layup or automated layup processes can be used. Laminates produced by such method can be oriented to enhance the strength of the material in a primary load direction. Therefore, as such, laminate orientation and thickness are highly crucial, having a direct influence on its mechanical properties. Although thickness is directly correlated with major mechanical properties improvement, orientation provides a quasi-isotropic layup, as mentioned above in 1.2.2.

As most manufacturing processes, layup processing has both advantages and disadvantages. Advantages are easy manufacturing, no big thermal, mechanical or chemical reactions involved, except for the resin cure. It has as disadvantages regarding the complexity of the part, as sole process, and investment value.

There are many factors that have to be considered while laying up, such as angling, defects (porosity, wrinkles, material excess or lack of material, etc.) and gaps. Porosity and wrinkles are consequence of lack of applied pressure during layup. Gaps are supposed to follow under rules, e.g. staggering, in order to have something that fulfills the gap in the next ply and improve part cohesiveness.

A.1.2.1 Hand Layup

Hand Layup is the process of manual layup and it is done mostly due to more small, intrinsic or complex geometries, where automated layup is not just able to perform. Highly qualified employees layup ply after ply with help of laser guidance and specialized tools as illustrated in figure A.1

The major drawbacks on this process are high labour costs, low production rates and variability (from laminator to another) [28]. One less known disadvantage of hand layup is the shearing while laminating (drape action is implied in hand layup of prepreg fabric)[29].

Figure A.1: Demonstration of shear while performing hand layup adapted from [29].

A.1.2.2 Automatic Layup - Automated Tape Layup

ATL is an automated layup machine which uses tape of carbon fiber prepregs, described in 1.2.1. A single tape of 150mm wide is usually used, although other sizes (300mm or 75mm) and combinations (single tape, double tape or multitape (four tapes) combination). Most manufacturers store layup material right above the roller head as ilustrated in A.2. ATL machinery had a development burst in 1980s, in terms of layup speed and 1990s, in terms of layup quality. [30]

This machine works using CNC programming, as well as AFP and Embraer's Waterjet cutting machine. As intended, gaps are induced and controlled within a range to reduce lost mechanical performance. Machine with 5 axes of freedom, has a head like one illustrated in A.2, where material is heated prior to layup, applying force through a roller to consolidate ply operation. Even as the one of the oldest automated layup processes [30], ATL is a very useful resource in aeronautic industry. However, AFP came as an improvement to ATL, allowing for more complicated geometries and fewer waste compared to ATL process.

A.1.2.3 Automatic Layup - Automated Fiber Placement

AFP machine was introduced in 1974 by Goldsworthy, being an ATL machine head with a slitting unit which slit tape into individual tows [32]. Commercially introduced in

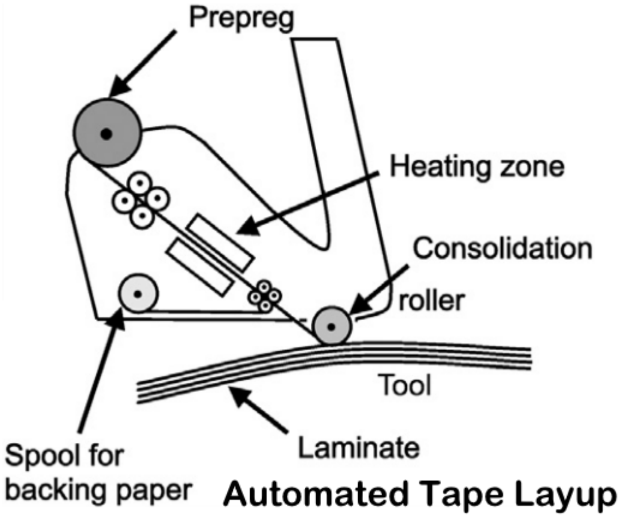


Figure A.2: Design of a common ATL head adapted from [31].

1980s, developed in the early 2000's, it's a machine with a with 6 axes of freedom, cooling material and warms where material is going to be laminated. The AFP machine head is exemplified at A.3, where some differences can be noted to the ATL machine head.

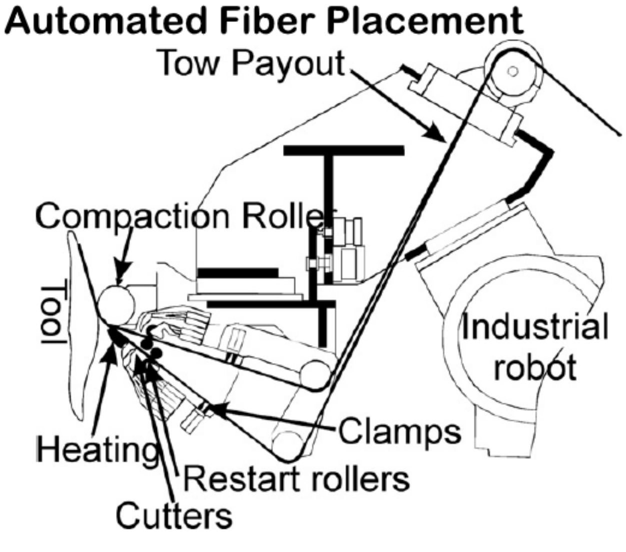


Figure A.3: Design of a common AFP head adapted from [30].

One of the differences in AFP to ATL processing is the material width. Whereas 150mm tape is the most common in ATL machine systems, 6,4 mm tow is the most common in AFP machine systems. The amount of tows is what characterizes the width of AFP lamination process, where some systems go up to 32 tows in a single sequence. Each tow is treated as one individual tow, allowing to cut, add and clamp one tow individually, allowing tow steering, for example. Tow width and number of tows depends highly on local geometry and complexity, providing us with the ability to adapt to these situations. AFP process productivity is lower than ATL rate since AFP normally is used to manufacture complex parts.

A.1.2.4 Autoclave cure and vacuum bagging

As depicted, it is necessary to cure CFRPs to end up with a finished and solid product. This process is usually done with the aid of a equipment called autoclave. Autoclave is, according to Kuppers J. and Walczyk, D.[33], a large pressure vessel that allows the simultaneous application of heat, vacuum within the bagged part and external pressure to the laminate. While being inefficient, it is the option that guarantees best quality product. This process requires the laminates to be within a vacuum bag to ensure part consolidation, obtained by vacuum system in autoclave which removes most volatile substances. This reduces porosity in the product. Vacuum bag also aids in pressurizing the product to assure a good, even product.

Autoclave process cycle combining temperature, pressure and vacuum is exemplified in figure A.4.

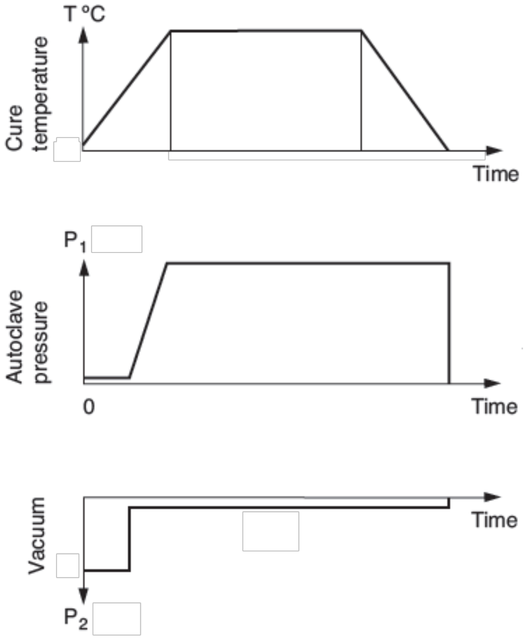


Figure A.4: Example of an Autoclave process cycle, adapted from [9].

A.1.3 CNC waterjet cutting and finishing

CFRP cutting is a very meticulous operation, due to the necessity of finishing with a clean cut and how hard it can be to cut carbon. With metallic blades, cut can be extremely hard since the cut would make the blade hot and that would damage the CFRP laminate through delamination where the blade would cut. Even with proper lubrication, the cut would be defined with scratches and probable delamination. This also ruins the blade and those designed to cut cured CFRP laminates are expensive. This results on a search to a clean cut using waterjet cutting machines. High pressure waterjet is focused to provide a cut with an error within a five tenths of a millimeter.This provides the shapely and crisp cut while preserving the dimensional integrity of CFRP products.

The machine is programmed and controlled via CNC programming, related to both

ATL and AFP machines as detailed in sections A.1.2.2 and A.1.2.3.

A.1.4 Quality Assurance

Quality assurance in Embraer is defined by a number of steps. Firstly, the parts are examined with an ultrassonic Non Destructive Test (NDT) for any signs of delamination and/or Foreign objects (FOs). Then, weighting and visual inspection are followed to ensure part normalization. As the last step of quality assurance, the product's order is reviewed to ensure all steps were made by a qualified and certified operator, while checking if all data is properly filled and completed.

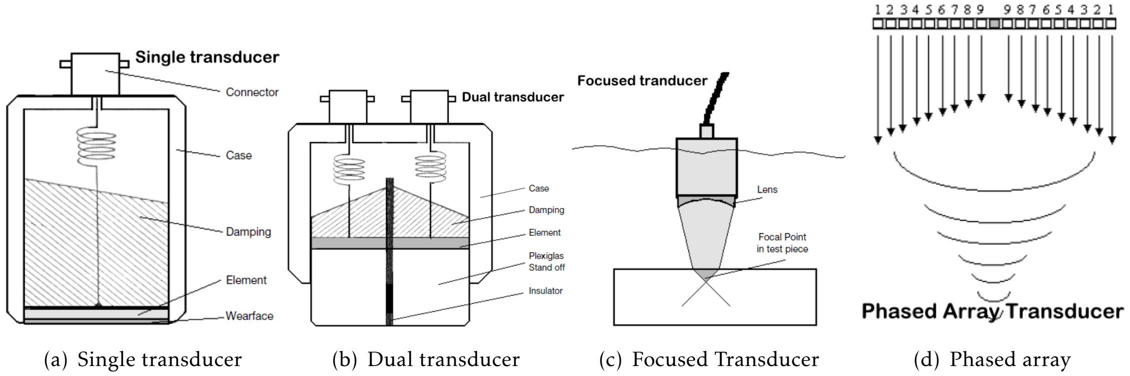
A.1.4.1 Ultrasonic NDT

Ultrasonic NDT is conducted by the operator using a ultrasonic NDT pulser/receiver through a transducer. While it acts as a very sensitive method to detect and accurately locate defects, it has its limitations. For example, it requires high-ceiling skill and training and relies on coupling medium to assure proper ultrasonic transmission [34].

There are many types of transducers, such as:

- Single Transducer;
- Dual Transducer;
- Focused Transducer;
- Phased Array.

While there are more types of transducers, these are the most used in Embraer's ultrasonic NDT. While single, dual and focused transducer work in a similar way (pulse and receive through the single or dual transducer), the phased array is mildly different. As the name suggest, the multiple transducers are pulsed through with a phased order. This allows focus on various depth of material.



(a) Single transducer (b) Dual transducer (c) Focused Transducer (d) Phased array

Figure A.5: The 4 main transducers used in Embraer Ultrasonic NDT, adapted from [34].

Kinetic reaction of cure

Assuming that the rate of heating is proportional to rate of reaction, like this:

$$\frac{d\alpha}{dt} = \frac{H(t)}{H_T} \tag{B.1}$$

We can assume that the equation can be split and defined by two separate equations, $K(T)$ and $f(a)$, which help us define reaction cure accordingly:

$$\frac{d\alpha}{dt} = K(T) \times f(a) \tag{B.2}$$

Nevertheless, heat dependence of the reaction rate is commonly defined as an Arrhenius equation, which is characterized as follows:

$$K(T) = A \exp\left(\frac{-E_A}{RT}\right) \tag{B.3}$$

When combined and defining heating rate as $\beta = \frac{dT}{dt}$, the cure rate can finally be defined as:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E_A}{RT}\right) f(a) \tag{B.4}$$

There have been multiple kinetic reaction models which fit cure reaction, Nonetheless, n^{th} order model, expressed in equation B.5, usually depicts thermoset cure behavior. Assuming a kinetic model and using equations above, cure reaction and its parameters can be predicted in a given temperature or heating rate. However, it requires isothermal analysis on different heating rates.

Using n^{th} order model, the final equation is presented as such:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E_A}{RT}\right)(1-\alpha)^n \tag{B.5}$$

2017 **Hot forming thermal cycle and material exposure effect on prepreg materials properties** **Tiago Correia**