Tiago Filipe Viegas Correia

Bachelor degree in Materials Science

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

Dissertation submitted in partial fulfillment
of the requirements for the degree of

Master of Science in
Materials Engineering

Adviser: Alexandre Velhinho, Associate Professor, NOVAFCT
Co-adviser: Filipe Silva, Process Engineer, Embraer Portugal - Estruturas em Compósitos, S.A.

FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

DRAFT: July 28, 2017

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

"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

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 preimpregnated with resin. As such, it is processed and transformed using molds, whether it is only deposited using either Automated Tape Laying (ATL) or Automated Fiber Placement (AFP) and also hot pressed into a shape. Since Embraer has such processes and there's a need to assess the materials response to its exposure and its response to being processes, a test proposal was made.

Accordingly, to answer this need, a test proposal is made in order to evaluate the material and the process. This provides a guide on how to make the necessary arrangements and how to conduct said tests. Furthermore, exposure conditions are disclosured as well as the size of the specimens and panels to process. In the end, we'll be able to understand how different exposure conditions and how hot drape thermal cycle affect this materials.

Keywords: hot drape, carbon fiber, exposure conditions, aeronautics, prepregs.

Independentemente da língua em que está escrita a dissertação, é necessário um resumo na língua do texto principal e um resumo noutra língua. Assume-se que as duas línguas em questão serão sempre o Português e o Inglês.

O *template* colocará automaticamente em primeiro lugar o resumo na língua do texto principal e depois o resumo na outra língua. Por exemplo, se a dissertação está escrita em Português, primeiro aparecerá o resumo em Português, depois em Inglês, seguido do texto principal em Português. Se a dissertação está escrita em Inglês, primeiro aparecerá o resumo em Inglês, depois em Português, seguido do texto principal em Inglês.

O resumo não deve exceder uma página e deve responder às seguintes questões:

- Qual é o problema?
- Porque é que ele é interessante?
- Qual é a solução?
- O que resulta (implicações) da solução?

E agora vamos fazer um teste com uma quebra de linha no hífen a ver se a LaTeX duplica o hífen na linha seguinte...

zzzz zzz zzzz zzz zzzz zzz zzzz zzz zzzz zzz zzzz zzz zzzz zzz zzzz zzz zzzz comentar-lhe zzz zzzz zzz zzzz

Sim! Funciona! :)

Palavras-chave: Palavras-chave (em Português) ...

Contents

List of Figures

List of Tables

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.

FTIR Fourier Transform Infrared.

ILSS Interlaminar Shear Strength.

ILTS Interlaminar Tension Strength.

RTA Room Temperature and Ambient conditioning.

Sign	Description	Unit
E_A	Activation Energy	$kJmol^{-1}$
$\frac{d\alpha}{dt}$	Degree of cure	
$H(t)$	Heat of the reaction at time t	
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	
$f(a)$	Reaction Model	
$K(T)$	Temperature dependent rate constant	
H_T	Total heat of the reaction	
R	Universal Gas Constant	$JK^{-1}mol^{-1}$

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 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.

However, 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 one 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 a mix between two 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 1.1).

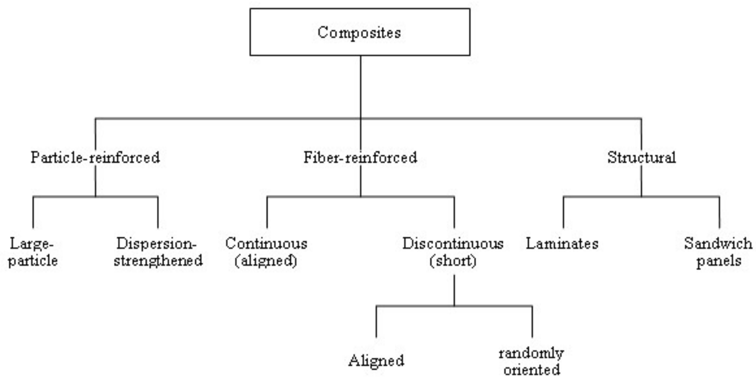


Figure 1.1: Reinforcement grouping adapted from [1].

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[2]. However, 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 [3].

1.1.1 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 1.2.4), one of the curing stages, to ensure better handling [4]

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. Since the mixture of resin, cure process starts to develop from room temperature. Slowing down the cure process is achieved by reducing the temperature (more information on section 1.2.4). 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[5].

Carbon fiber range of applications vary depending on which precursor polymer is used, with many precursors being studied to produce carbon fiber while easy conversion to carbon fiber, high carbon yield and cost-effective processing being the main searched characteristics of the precursors used[2]. The most popular precursors used are:

1. **Acrylic precursors** - Which have been the most successful in the industry world, with PAN being the most popular acrylic precursors for quite some time now;
2. **Cellulosic precursors** - While containing around 44% carbon, the process is more than simple dehydration, like Edison's filaments, and the carbon yield is only around 25%.
3. **Pitch-based precursors** - In spite of having a 85% carbon yield, these precursors give carbon fiber a high modulus, due to the graphical nature of these fibers, although the fibers have poorer compression and transverse properties compare to Acrylic precursors.

Other precursors, like Vinylidene chloride and phenolic resins are used as well, but were found not commercially viable.

1.1.1.1 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. However, 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[6]. This is justified by several reasons:

1. Low volume reduction after cure, therefore 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 [6]. 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 a group of 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 1.2.4.

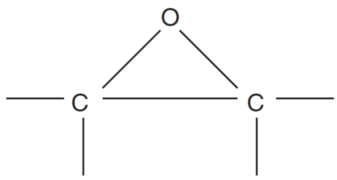


Figure 1.2: Illustration of a three member ring epoxy group. [6]

1.1.2 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 1.2.2). The carbon fiber continuos reinforcement will provide strength in the orientation of said fibers. However, in the perpendicular direction, 90°, load is absorbed by the matrix, therefore, strength is characterized by the matrix, which is notoriously weaker. Therefore, it is logical to design a laminate containing fibers oriented in multiple directions. Campbell [2] defines a quasi-isotropic laminate as a balanced laminate with equal number of plies in the 0°, +45°, -45° and 90°. This proposal is highly regarded as optimal, since it provides laminates with great strength in multiple orientations.

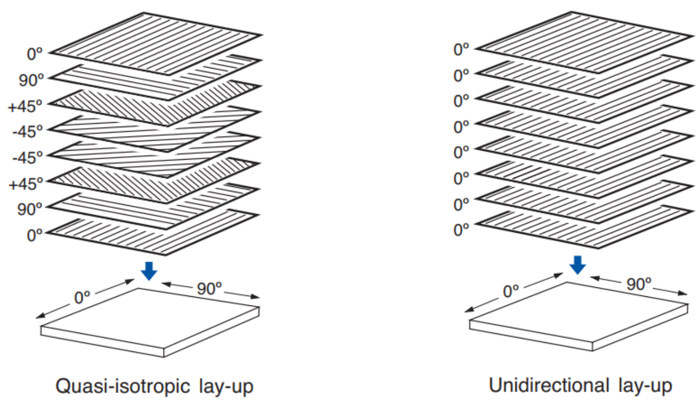


Figure 1.3: Orientations in a laminate and an example of a quasi-isotropic laminate adapted from [7]

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 the fibers from deforming under compression. A summary is provided in table 1.1. [2]

Table 1.1: Summary of dominating composite constituent on each mechanical properties, adapted from [2].

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

1.2 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.

1.2.1 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.

1.2.2 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 1.1.2.

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.

1.2.2.1 Hand Layup

Hand Layup is the process of manual layup and it's done mostly due to more small, intrinsic or complex geometries, where automated layup isn't just able to perform. Highly qualified employees layup ply after ply with help of laser guidance and specialized tools.

The major drawbacks on this process is high labour costs, low production rates and variability (from laminator to another) [8].

1.2.2.2 Automatic Layup - Automated Tape Layup

Automated Tape Layup (ATL) is an automated layup machine which uses tape of carbon fiber prepregs, described in 1.1.1. 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 1.4. ATL machinery had a development burst in 1980s, in terms of layup speed and 1990s, in terms of layup quality. [9]

This machine works using CNC programming, as well as Automated Fiber Placement (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 1.4, 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 [9], 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.

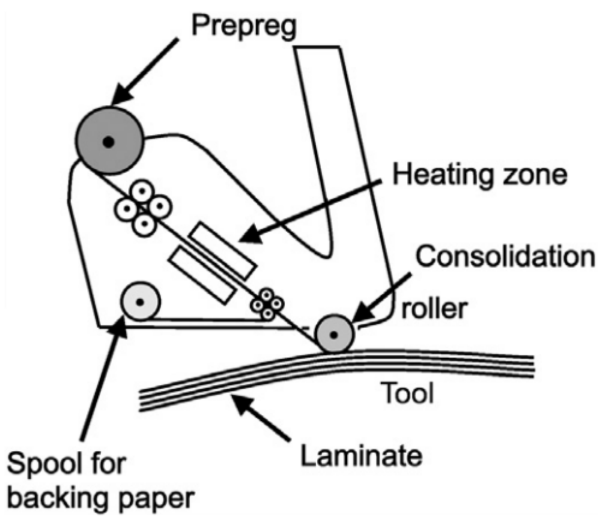


Figure 1.4: Design of a common ATL head adapted from [10].

1.2.2.3 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 [11]. Commercially introduced in 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 1.5, where some differences can be noted to the ATL machine head.

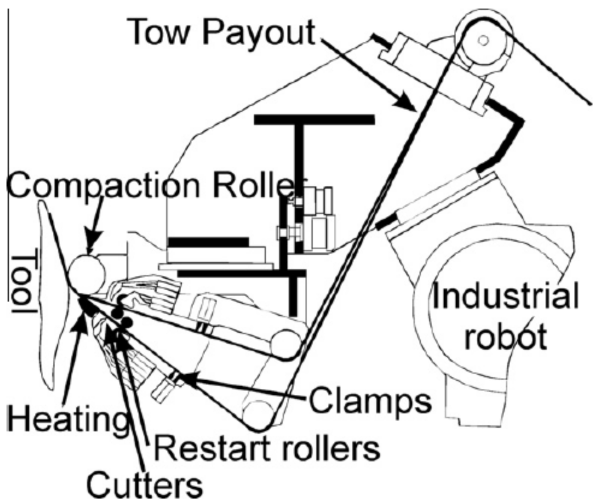


Figure 1.5: Design of a common AFP head adapted from [9].

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.

1.2.3 Hot forming process

Hot forming is a mechanical process which forms the material to a mold using both temperature and pressure as auxiliary 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. 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 tool 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.

1.2.4 Cure

The epoxy resin cure is defined in three different stages [4]:

- 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 -18ºC.
- 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 two different reactions occur in this specific case an amine curing agent. First there's a reaction between the primary amine group hydrogen and the carbon in the epoxy group. Then, the secondary amine group hydrogen bonds with carbon in epoxy group. This reaction is exemplified in figure 1.6.

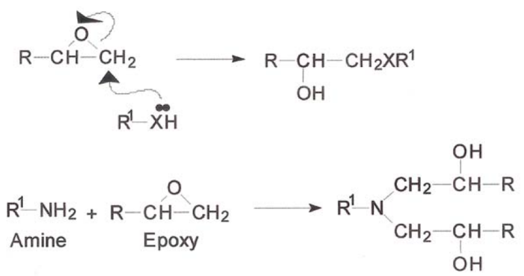


Figure 1.6: General cure process for epoxy resins using amine curing agent. [6]

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 most used to characterize thermoset polymers (i.e. epoxy resin). Kinetic parameters of cure reaction can be found through DSC analysis. Adapting and citing Hardy [12], data gathered from DSC equipment can be fitted into kinetic reaction models. Assuming that the rate of heating is proportional to rate of reaction, as written below:

$$\frac{d\alpha}{dt} = \frac{H(t)}{H_T} \tag{1.1}$$

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

$$\frac{d\alpha}{dt} = K(T) \times f(a) \tag{1.2}$$

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

$$K(T) = A\exp\left(\frac{-E_A}{RT}\right) \tag{1.3}$$

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

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(\frac{-E_A}{RT}\right)f(a) \tag{1.4}$$

There have been multiple kinetic reaction models which fit cure reaction, however, n^{th} order model, expressed in equation 1.5, 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.

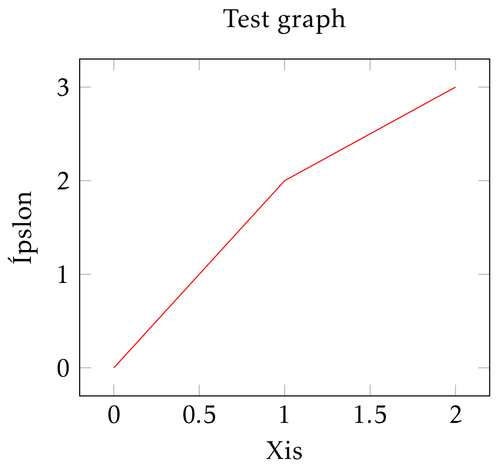
Using n^{th} order model, the final equation is presented as such:

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(\frac{-E_A}{RT}\right)(1-\alpha)^n \tag{1.5}$$

1.2.4.1 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. <inserir referência>, a large pressure vessel that allows the simultaneous application of heat, vaccum 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,



1.2.5 CNC waterjet cutting and finishing

1.2.6 Quality Assurance

2.1 Requirements and properties

Materials requirements are defined in standard MEP 15-047 for the ATL material, table 2.1 and MEP 15-067 for the AFP material, table 2.2.

Table 2.1: Physical and Mechanical Requirements for ATL material

Mechanical Requirements				
Property	**Test temperature and environmental condition**	**Stregth Requirement [MPa]**		**Modulus Requirement [GPa]**
		Min. Average	**Min. Individual**	
Interlaminar 0º Direction	RTA	103	96	N.A.
	ETW	63	59	N.A.
Interlaminar Tension Strength	RTA	TBD	TBD	TBD
	ETW	TBD	TBD	TBD

Physical Requirements		
Property	**Requirement**	**Unit**
Laminate Thickness per Ply	0,184 ± 0,020	[mm]
Fourier Tranform Infrared (FTIR)	Informative	N.A.
Differential Scanning Calorimetry (DSC)	Informative	N.A.
Differencial Mechanical Analysis (DMA)	T_g(dry) = 210	[ºC]

Table 2.2: Physical and Mechanical Requirements for AFP material

Mechanical Requirements				
Property	**Test temperature and environmental condition**	**Stregth Requirement [MPa]**		**Modulus Requirement [GPa]**
		Min. Average	**Min. Individual**	
Interlaminar 0º Direction	RTA	88,1 (13)	77,2 (11)	N.A.
	ETW	60,1 (9)	52,6 (8)	N.A.
Interlaminar Tension Strength	RTA	TBD	TBD	TBD
	ETW	TBD	TBD	TBD

Physical Requirements		
Property	**Requirement**	**Unit**
Laminate Thickness per Ply	0,191 ± 0,010	[mm]
Fourier Tranform Infrared (FTIR)	Informative	N.A.
Differential Scanning Calorimetry (DSC)	Informative	N.A.
Differencial Mechanical Analysis (DMA)	T_g(dry) = [210;230]	[ºC]

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, but due to time constraints it was not possible to arrange such testing conditions.

- **RTA** - Temperature at 23ºC ± 3ºC, 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 test 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: Evaluate the prepreg after hot drape thermal cycle and exposure conditions. These tests will be the ones to give us the mechanical properties after the co-cure. It'll be important to assess the effects of the thermal cycle, together with material exposure.

- ILSS
- Interlaminar Tension Strength (ILTS).

2.3 Material exposure conditions

The material exposure conditions are expressed in table 2.3. 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 2.3: 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] 2 days of available of 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 4 and 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.

Material selection - Roll number, batch, exposure.

Vacuum bag

Lamination programs

Lamination problems

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 2.3, 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 15 specimen. However, because of some constraints regarding panel quality mentioned in section 2.4, some panels sample size were reduced.

2.4.1.1 Specimen nomenclature

In order to facilitate specimen identification and testing, specimens were identified using the following nomenclature:

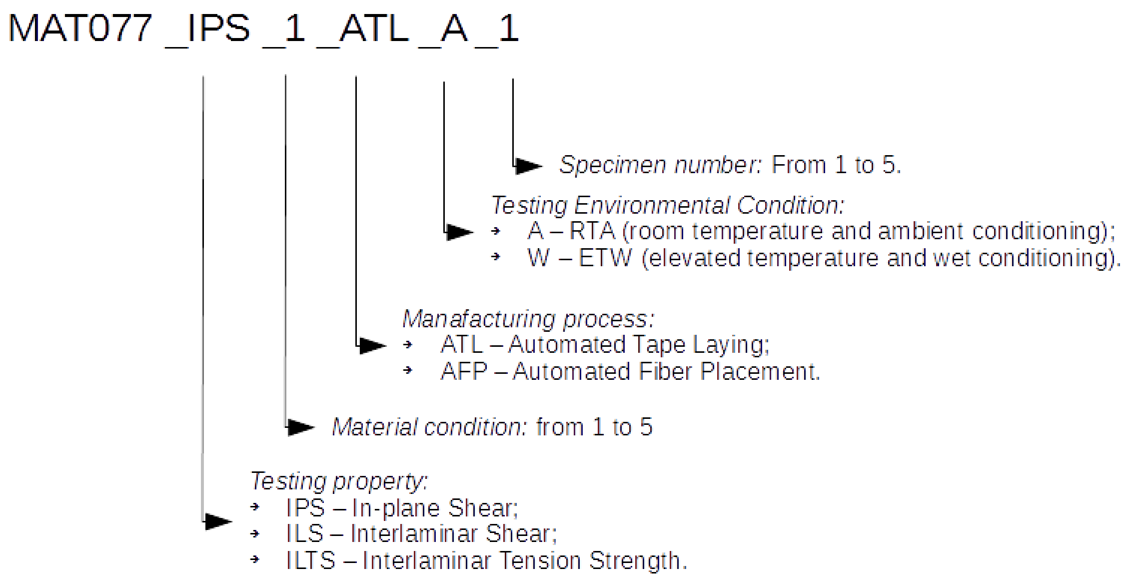


Figure 2.1: Specimen naming code.

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'll allow us to determine if the laminate is consistent in its full extent, as well as determine if there's defects in the laminate. Normalized cured ply thickness and/or fiber volume fraction will be used for most lamina level tension and compression strength and modulus properties normalization. Lamina level properties that wont be normalized include in-plane shear strength, modulus and Poisson's ratio, since data scatter should reduce or remain the same. If data scatter increases significantly after normalizing, the reason must be investigated. Wherever properties are normalized, both measured and normalized data will be considered.

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:

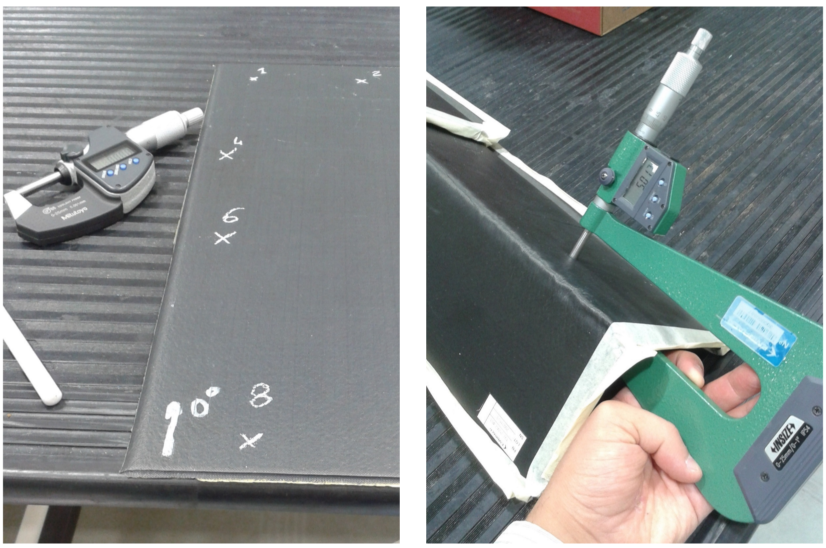
$$T_p = \left(\frac{\frac{t_1}{N_p} + \frac{t_2}{N_p} + \frac{t_3}{N_p} + \ldots + \frac{t_i}{N_p}}{n_m} \right) \tag{3.1}$$

In accordance with equation 3.2, the average nominal thickness from the panels is used to obtain the nominal thickness:

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

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

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's more in the prepreg than necessary, 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

The samples are prepared according to ASTM E168 by withdrawing the resin of the prepreg, with reagent grade methylene chloride at room temperature and then the fibers are manipulated in order to ensure full resin withdraw. The resin/reagent mix is then placed on a salt block and the solvent is evaporated. The resulted resin is then tested in a certified FTIR tester.

3.2.2 Results and discussion

3.3 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.

3.3.1 Procedure

3.3.2 Results and discussion

3.4 Dynamic Mechanical Analysis

[13]

3.4.1 Procedure

3.4.2 Results and discussion

Mechanical testing of cured laminates

4.1 Interlaminar Shear Strength

Interlaminar shear test shall be done according EN 2563 for ATL material and ASTM D2344 for AFP material. 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	$(6 * t \pm 0{,}25)$ x $(2 * t \pm 0{,}2)$	12

4.1.1 Specimen preparation

4.1.2 Test and machine preparation

4.1.3 Results and discussion

4.2 Interlaminar Tension Strength

Interlaminar Tension Strength shall be done according to ASTM D6415, in which the specimens are stated for both ATL and AFP material, in figure 4.1. 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 (more on detail in annex):

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.

ILTSpecimens shall be cut by disk cutter thanks to the imposed 90º 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, with the nuance that an excess would be added, providing room to sanding the excess and assure specimen quality.

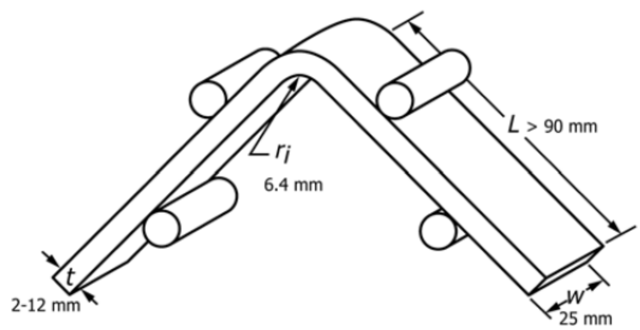


Figure 4.1: Dimensions for ILTS specimens [14]

4.2.1 Specimen preparation

4.2.2 Test and machine preparation

4.2.3 Results and discussion

[1] *Materials selection*, 2017. [Online]. Available: `http://www.phy.cuhk.edu.hk/orientationday/materials.htm`.

[2] F. C. Campbell, *Manufacturing Processes for Advanced Composites*. Elsevier Ltd, 2004, vol. 1.

[3] ASTM Standard D3878-07, "Standard Terminology for Composite Materials," vol. 07, no. Reapproved 2013, pp. 1–5, 2013.

[4] U. Federal Aviation Administration of Departement of Transportation, *Aviation maintenance technician handbook-airframe*. United States Department of Transportation, Federal Aviation Administration, 2012, vol. 1.

[5] P. Morgan, *Carbon fibers and their composites*. Taylor & Francis Group, LLC, 2005.

[6] D. Ratna, *Handbook of Thermoset Resins*. iSmithers – A Smithers Group Company, 2009.

[7] H. Composites, *Prepreg technology*. 2013.

[8] J. D. Skramstad, "Evaluation of hand lay-up and resin transfer moulding in composite wind turbine blade manufacturing," Master's thesis, Montana State University-Bozeman, 1999.

[9] D. H.-J. Lukaszewicz, C. Ward, and K. D. Potter, "The engineering aspects of automated prepreg layup: History, present and future," *Composites Part B: Engineering*, vol. 43, no. 3, pp. 997–1009, 2012.

[10] B. Astrom, *Manufacturing of polymer composites*. Taylor & Francis, 1997.

[11] W. Goldsworthy, "Geodesic path length compensator for composite-tape placement method," U.S. Patent 4 627 886, 4th April 1971.

[12] R. Hardis, "Cure kinetics characterization and monitoring of an epoxy resin for thick composite structures," Master's thesis, Iowa State University, 2012.

[13] K. P. Menard, *Dynamic mechanical analysis*, 2nd ed. Taylor & Francis Ltd., 2008.

[14] ASTM International, "ASTM D6415/D6415M-06a (Re2013) Standard Test Method for Measuring the Curved Beam Strength of a Fiber-Reinforced," *Annual Book of ASTM Standards*, no. Reapproved 2013, pp. 1–10, 2013.

2017 4.2.3 **Tiago Correia**