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Development of an LCM process for rapid curing CFRP parts

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Abstract

In the last few years, composite materials parts have seen a huge increase in utilization in different industrial sectors such as the automotive or the aerospace, competing with the most commonly used steel, aluminum or titanium alloy. It is due to the possibility of obtaining good performances in terms of load resistance with lightweight structures.

Obviously, the negative aspects of this type of materials are their high cost, poor surface resistance and the difficulties in reparing.

The goal of this project is to study a process used to realize composite material parts and to optimize it according to the defects of the parts obtained.

In particular, the process analyzed is the liquid compression molding (LCM) which is commonly used for a rapid curing carbon fibre/epoxy material system, a candidate material for automotive structural applications.

The manufactured parts have been characterized by defects using microscopy and mechanical tests have been performed to gauge performance. Thanks to that it has been possible to understand the relationship between various processing parameters and part quality.

1. Composite Materials

1.1 Introduction

A composite is a structural material made of two or more parts not soluble in each other: the reinforcing phase and the matrix.

The reinforcing phase could be in the form of fiber, particles or flakes; the matrix is usually continuous.

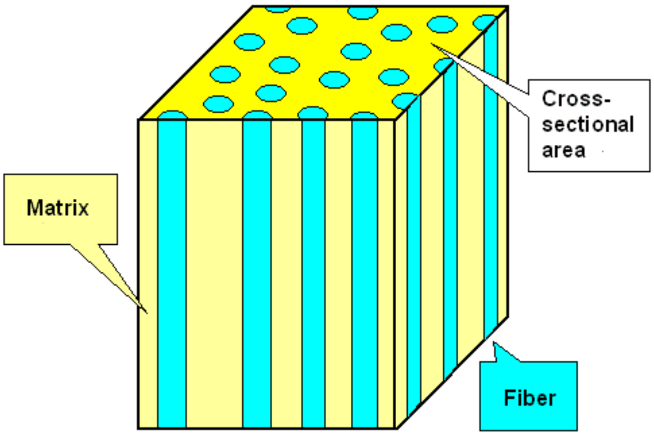


Figure 1-Composite Material structure

The main characteristics of reinforcing fibers are:

- the smaller the diameter, the lower the probability of defects (size effect);
- the strong direction is aligned along the fiber axis;
- the high aspect ratio (l/d);
- the high degree of flexibility.

The main aspects, instead, of the matrix are:

- transfer loads to the fibers;
- provide lateral support to limit the fiber buckling;
- hold the fibers in the desired orientation;
- provide the final shape;
- protect fibers from degradation.

The most common fibers are carbon, glass, Kevlar, boron, and Alumina, while the matrix could be in polymer, metal or ceramic.

The use of the 2 phases allows to obtain physical e chemical properties wich are better of the single-phase taking the advantages from each one.

Furthermore, it is possible to manage the orientation of the reinforcing fibers in order to have a bigger resistance in certain direction.

On the other hand, the most common drawbacks for this kind of material are:

- High cost of fabrication: a panel made of graphite and epoxy could cost even 10 times than the cost of the single material;
- Mechanical Characterization: composite is not isotropic so the properties are different in each part of the piece so many parametres are necessary for this goal;
- Repair composite is really difficult in comparison with metal. This is due to the phase constituents the material.

1.2 Parameters

It easy to understand that the quality and the main characteristics of the composite are mostly influenced by the fibers and in particular by:

- type of fiber;
- shape of the fibers;
- fibers volume fraction;
- technology used fort the production.

Each one has its own importance and has to be analyzed to obtain a component able to satisfy the different necessities.

1.2.1 Material

Obviously, the type of material influences the final characteristics of the composite: every material has its own stiffness and resistance. Fibers are generally expected to have a high elastic module and strengths. This expectation and cost have been key factors in the carbon, aramids, and glass dominating the fiber market for composites.

In the table below are given the typical properties of these materials:

Table 1-Typical properties fibers

	Carbon	Aramid	Glass
Young's modulus [GPa]	230	125	85
Ultimate tensile strength [MPa]	2000	1400	1550
Axial coefficient of thermal expansion [µm/m/°C]	-1.3	-5	5

1.2.2 Shape of fibers

The shape and type of fiber determine the behaviour of the final composite: for examples with flakes we have an isotropic material not given with unidirectional fibers.

Furthermore, the mechanical properties like tensile strength and modulus are influenced by the fyber type, length and arrangement.

There are many ways to design the structure: fibers can be continuos or discontinuous in length and arranged in unidirectional, bidirectional, multidirectional, or completely random orientation. It is also possible to have a combination of these arrangements.

In the picture below are shown some fibers orientation possibility:

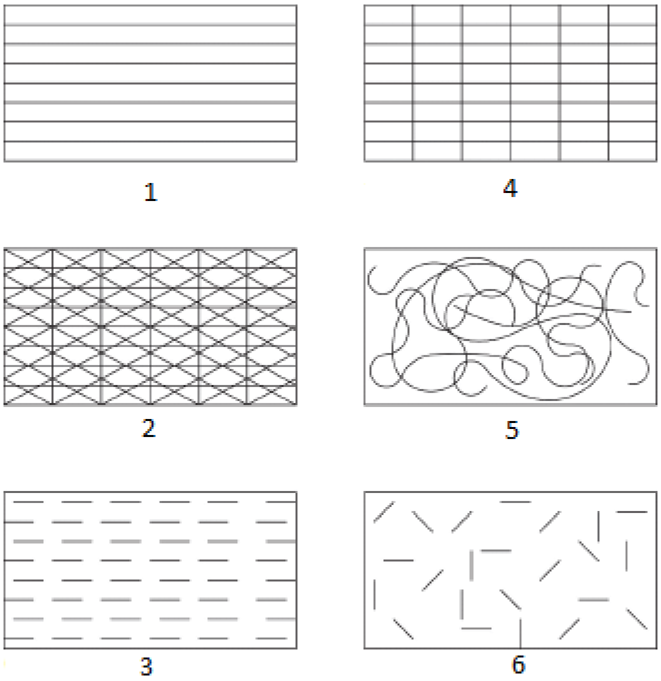


Figure 2-Fibers orientation

These are 1 unidirictional continuos, 2 multidirectional continuos, 3 unidirectional discontinuos, 4 bidirectiona continuos, 5 randoma continuos, 6 random discontinuos.

1.2.3 Fibers Volume Fraction

Fibers volume fraction is the percentage in volume of the fibers in the entire volume of the composite. This parameter is very important for the mechanical properties of the part by the fact that fibers are responsible for the stiffness, flexibility and so on.

Usually, fiber volume fraction is indicated with V_f and it is given by the relationship:

$$V_f = 1 - V_m - V_{voids}$$

Where V_m is the matrix volume ratio, V_{voids} is the voids volume fraction. The steps to calculate the fibre volume fraction are the following (Heslehurst, 2005).

To determine V_m is possible to use the relationship below:

$$V_m = \frac{1}{1 + \left(\frac{V_{fibre}}{V_{resin}}\right)}$$

Where V_{fibre} and V_{resin} are given by:

$$V_{fibre} = \frac{W_{fibre}}{\rho_{fibre}}; \ V_{resin} = \frac{W_{resin}}{\rho_{resin}}$$

Having indicated with W the weight and with ρ the density.

The determination of V_{voids} will be explained in paragraph 4.1.

Common values of the fibers volume fraction are between 0,5 and 0,7.

The ASTM method requires the destruction of a small sample, but it is possible to follow different approaches as explained in paragraph 4.2.

1.2.4 Technology for production

Another fundamental aspect is technology used for the production. It can influence the presence of voids and the quality of the pieces.

There are many differences between the processes for metals and those for composites like pressure which is lower with composite, and the waste of material.

The type of process depends on the matrix: if it is a thermoset, the most common are Resin Transfer Molding (RTM) with all its variants (HP-RTM, VARTM,…) or Compression molding and Injection Molding for thermoplastic.

In these processes, fibers and matrix are directly combined in the mould or on the tool to make the composite part.

The thermoset plastics are subjected to a necessary process to pass from the liquid state to the solid: the curing step. It is realized thanks to heat which activates a chemical reaction between the bonds of the resin.

The thermoplastic, instead, does not need any chemical reaction but just a cooling phase to solidify.

Many authors (Kesarwani, 2016) classified composite processes according to one main aspect: the mould. Processes can be divided in open mold process or closed mold process.

Among the open mold, the laminates are exposed to the atmosphere during the process, are wet lay-up process, Spray-up process, Pultrusion or filament winding.

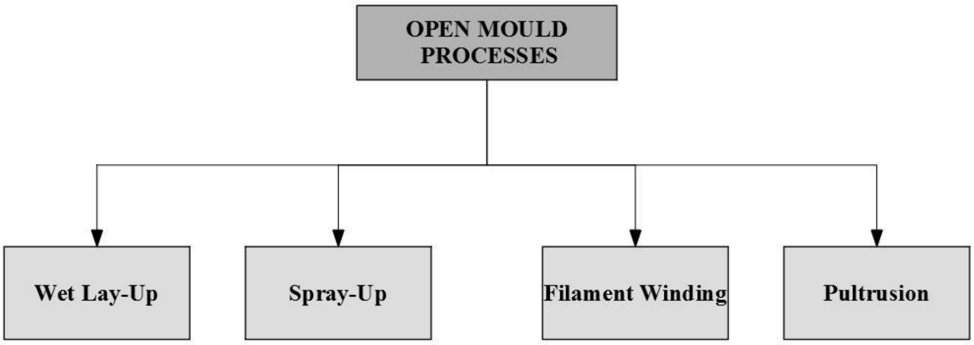


Figure 3-Open Mould Processes

While, among the closed mold, in which the laminates are manufactured in a mold or in a vacuum bag, are: Resin transfer molding, Vacuum-assisted Resin transfer Molding, Compression Molding, Structural Reaction Injection Molding, Compression Resin Transfer Molding, Injection Molding, Prepreg Lay-up, Roll Wrapping and Liquid Compression Molding.

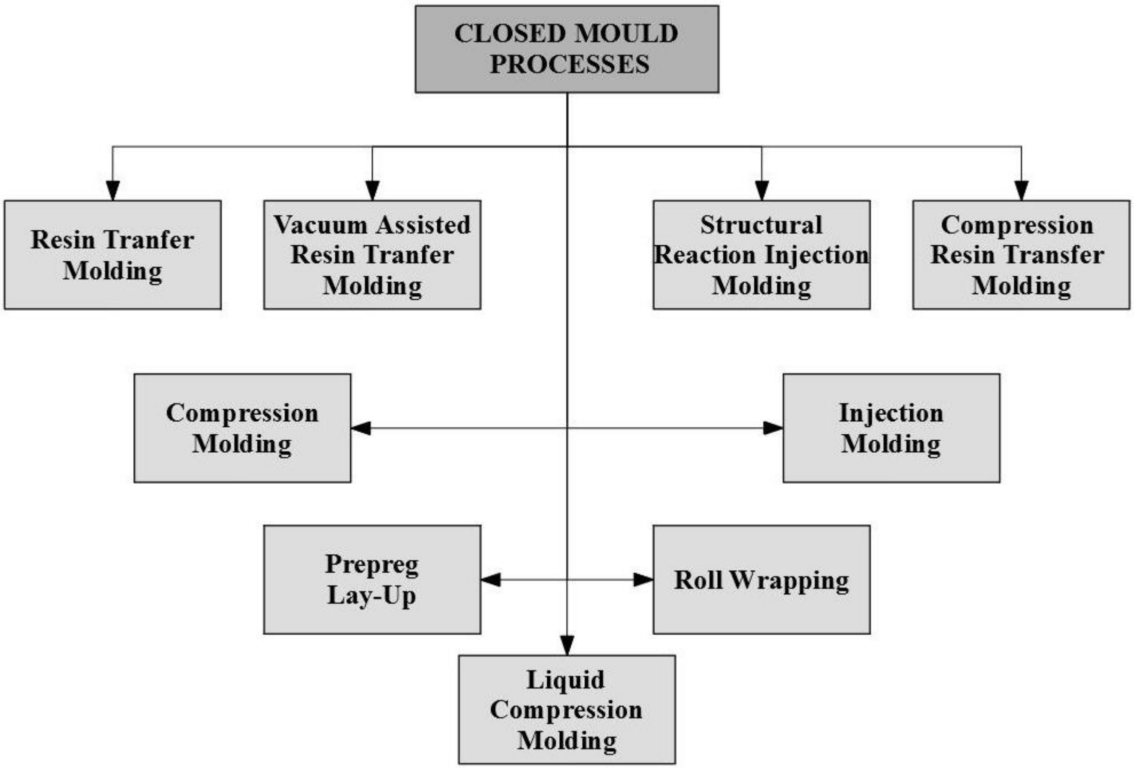


Figure 4-Close Mould Processes

1.3 Classification of composites

Composite materials are usually classified according to three main features: type of matrix, type of fibers and reinforcement form.

- The polymer composites can have as matrix a thermoset or a thermoplastic.

The most common thermoset polymer for composite materials are shown in the picture below:

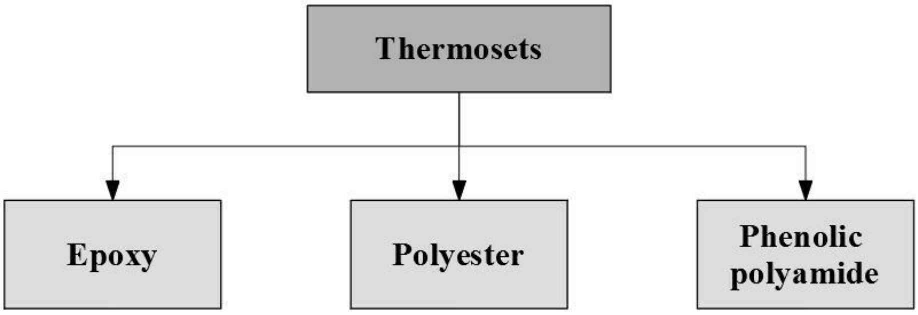


Figure 5- Thermosets in composites

Among the thermoset composites are Epoxy, Phenol polyamide and Polyester materials.

The thermoplastic composite is usually more than the thermoset:

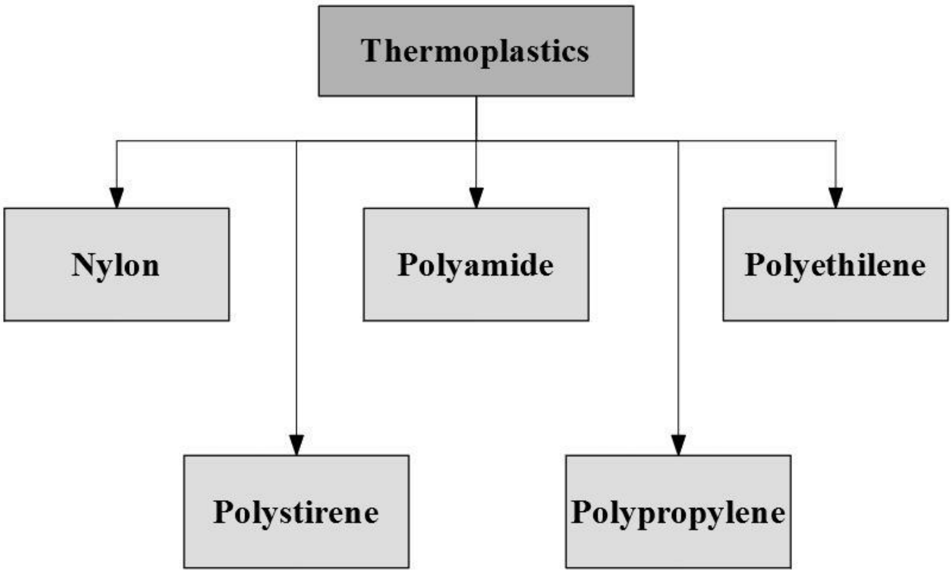


Figure 6-Thermoplastics in composites

So, these are Polyethylene, Polystyrene, Polyamides, Nylons and Polypropylene.

The classification made by the type of fibers is based on the reinforcement form. Parts could be defined as fibre reinforced composites, laminar composites and particulate composites. Fibre Reinforced composites (FRP) can be further divided into those containing discontinuous or continuous fibres:

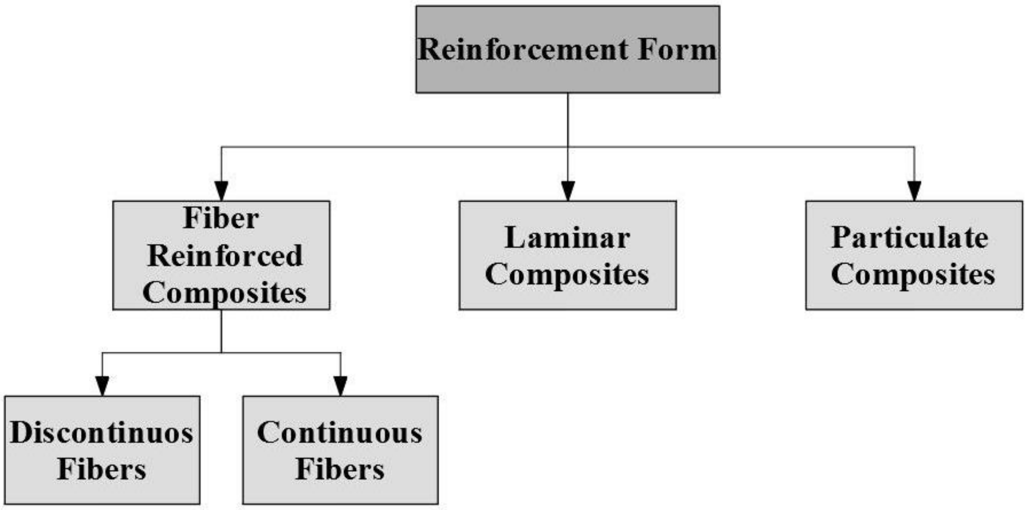


Figure 7-Reinforcement form

- **Fibre Reinforced Composites** are composed of fibres embedded in the matrix material. Such a composite is considered to be a discontinuous fibre or short fibre composite if its properties vary with fibre length. On the other hand, when the length of the fibre is such that any further increase in length does not further increase, the elastic modulus of the composite, the composite is considered to be continuous fibre reinforced. Fibres are small in diameter and when pushed axially, they bend easily although they have very good tensile properties. These fibres must be supported to keep individual fibres from bending and buckling.

- **Laminar Composites** are composed of layers of materials held together by the matrix. Sandwich structures are under this category.

- **Particulate Composites** are composed of particles distributed or embedded in a matrix body. The particles may be flakes or in powder form. Concrete and wood particle boards are examples of this category.

Focusing on the continuous or discontinuous fibers, they can bring obviously to isotropic or orthotropic behaviour. Usually, the continuous fibers are called long fibers while the discontinuous are called short fibers.

Long fibers can bring to unidirectional, bidirectional or spatial reinforce:

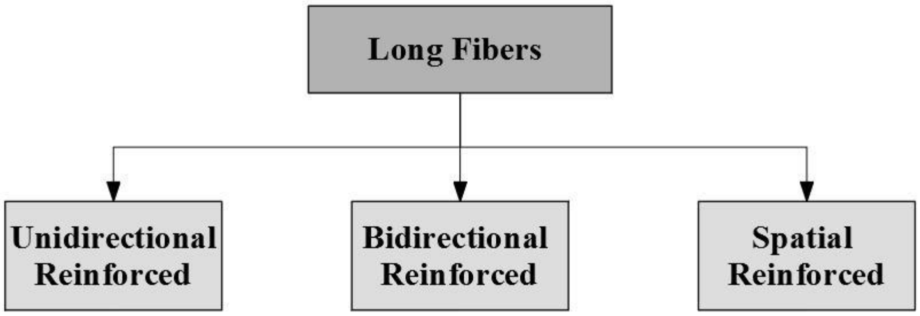


Figure 8-Long fibers reinforcement

While short fibers bring to random reinforced or preferred reinforced:

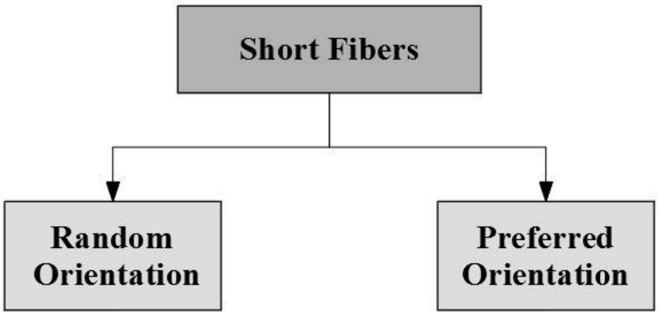


Figure 9-Short fibers reinforcement

1.3.1 Laminate

A laminate is defined as a material made of the overlapping of different layers which could be unidirectional or not and this gives the mechanical properties of the laminate. For this reason, a standard laminate code has been recognizing and it is defined by the following detailed description (Adams, 2002):

1. The first ply to be listed is that one laid up, and after that, the other are listed is the sequence. The square brackets indicate the beginning and the end of the layers.
2. Different subscripts capital letters are used to indicate different meanings: the capital T is used to say that the total laminate is shown; the capital S is used for symmetrical panels and indicates that is shown just half of the plies; the capital Q is used for antisymmetric laminate.
3. The number in the square brackets indicates the orientation of each layer in degrees according to the x-axis of the laminate.

4. If there are many plies with the same properties and orientation and they are adjacent, a subscripted number, which represents the orientation of the plies, can be used.

5. If the 2 identical plies have a different orientation or a different material, they are separated by a slash.
6. If 2 adjacent plies have the same difference of angle but with the opposite sign, plus or minus are used to describe it. Plus or minus are used instead of the numerical subscript and each sign represents one ply.
7. If there are sequences of plies which are repeated, is used the name Set. The sets follow the same rules of the plies.
8. If there are some plies with different material or thickness, to describe this situation a different subscript is used with each ply angle.

1.4 Carbon fiber epoxy material system

The material focused on this study is a carbon fiber-reinforced plastic composite (CFRP), specifically a carbon fiber non-crimp fabric (NCF) and epoxy composite so made of carbon as the reinforcing phase and a thermosetting polymer as a matrix.

Carbon Fibers

The carbon fibers give to the parts high tensile, low density, low thermal expansion, high abrasive resistance.

From the other hand they could be really expensive for the manufacturing problems and usually they are used in the sectors like aerospace or automotive which requires high strength to weight ratio. The main drawback of this kind of material is that is not easy to define a fatigue endurance limit as for the metals. For that reason usually, are required high safety margins in the applications.

Here there is an image of a typical carbon fiber composite part, in this case, a unidirectional plate:

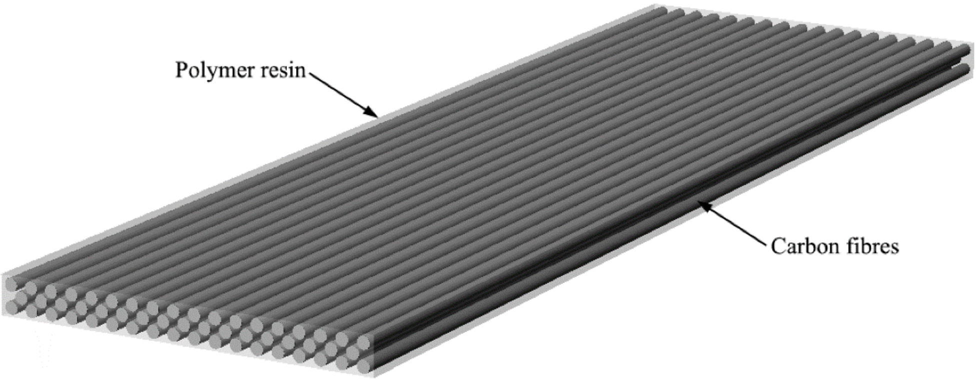


Figure 10-CFRP structure (Liu, 2015)

As said before, the reinforcement is the responsible to strength and rigidity of the composite material and two important variables to determine the elastic modulus and stress are the layout of carbon fiber and the proportion between fiber and matrix.

Carbon fibers are obtained starting from a polymeric precursor (the most widespread is PAN - Polyacrylonitrile, but there are also rayon and pitch) subjected to controlled oxidation, carbonization or graphitization processes, based on the desired mechanical characteristics. The fibers obtained by carbonization, in fact, have high mechanical strength but lower than those obtained by graphitization. Hence the difference between high-strength carbon fibers and high modulus carbon fibers.

A possible classification based on the properties of carbon fibers is:

- Standard Modulus (SM);
- Intermediate Modulus (IM);
- High Modulus (HM);
- Ultra High Modulus (UHM).

The properties for each group are expressed in the table below:

Table 2-Classification of carbon fibers composites

	Tensile Elastic Modulus [GPa]	**Tensile Strength [MPa]**
Standard Modulus	200-250	2500
Intermediate Modulus	250-350	3500
High Modulus	350-500	2500
Ultra High Modulus	>500	2500

In polymeric composites, carbon fibers are used as fabric. Fabric is a manufactured assembly of long fibers usually in form of a sheet by which is possible to produce a laminate with many layers.

Here is an example of a carbon fabric:

Figure 11- Carbon fabric

The term Non-Crimp Fabric (NCF), instead, refers to a unidirectional fiber plies kept together by stitching yarns. The use of NCF is necessary to minimize the time production and decreases, of course, the costs. It is due to the simplification of the process to manufacture laminates obtained by the use of this kind of fabric. So, this structure leads to an advantageous combination of high material properties, low-cost processing, and excellent drape performance so it is also suitable for molding composite materials of complex shape.

NCF has been used used mostly in automotive applications thanks to some good advantages like good drappability and good mechanical properties because the tows are not crimped or woven (Dry Composites, 2014).

1.4.1 Manufacturing of carbon fibre

The process to fabricate carbon fibers is expressed by many authors (Huang, 2009). The precursor of carbon fibers is PAN (polyacrylonitrile), a linear polymer with carbon and nitrogen groups.

The process to fabricate fibers consists of 5 different steps:

1. Spinning: This is a very important part of the process because it helps to form the internal atomic structure of the fibers. The powder of Acrylonitrile is mixed with methyl acrylate or methyl methacrylate, and thanks to the reaction with a catalyst in a polymerization process the polyacrylonitrile are formed. Suddenly, the plastic is spun into fibers with many methods: the plastic can be mixed with chemicals and pumped into a bath where it becomes solid; the plastic can be heated and pumped into a chamber to let evaporate the solvents. After that, the fibers are washed and stretched to align the molecules and to provide the formation of bonds between the carbon crystals.

2. Stabilizing: This process is necessary to improve the bonding between the crystals from a linear bonding to a more thermally stable and it could be done altering chemically the fibers. The fibers are heated between 200 to 300° C for 30 to 120 minutes and thanks to that, they rearrange the bonding with the oxygen from the air. It is a very complex process which requires many equipment and techniques like a series of heated chambers or hot rollers or a tool to mix air with gases to accelerate the stabilization.

3. Carbonization: The fibers after the stabilizations are heated in a furnace at a high temperature, between up to 3000 ° C in a chamber without oxygen to prevent their burning. The high temperature helps to expel the non-carbon atoms like water vapour, ammonia, carbon monoxide, carbon dioxide, hydrogen, nitrogen and in the meanwhile the atoms of carbon which remain in the fibers form tightly bonded crystals aligned parallel to the long axis.

4. Treating: At the end of the carbonization process, the fibers have a bad surface to be used as reinforcing of a composite part because it does not bond well with plastics. To improve this defect, the fibers are oxidized. The oxidation gives a better chemical and mechanical bonding properties. It is done immersing the fibers in a bath of gases like air, carbon dioxide, ozone or in a bath of liquids like sodium hypochlorite or nitric acid. The treating process could be done also electrolytically using them as a positive in a bath of conductive materials.

5. Sizing: The last part of the process is coating the fibers to protect them from damages and the materials used in this step must be compatible with the adhesive used to form composite materials. The coated fibers are wound onto cylinders called bobbins which are loaded into a spinning machine and the fibers are twisted into yarns of various sizes.

Polymer Resin

The resins (plastics or elastomers) are polymers by which are produced objects thanks to the combined action of heat and/or pressure in forming processes.

The polymers are made up of more or less long chains, linear or variously branched, in which the monomer or monomers relate to the repeating unit that repeats many or thousands of times.

From the point of view of the monomers used for the production of the polymer are:

- homopolymers: consisting of a single type of monomer

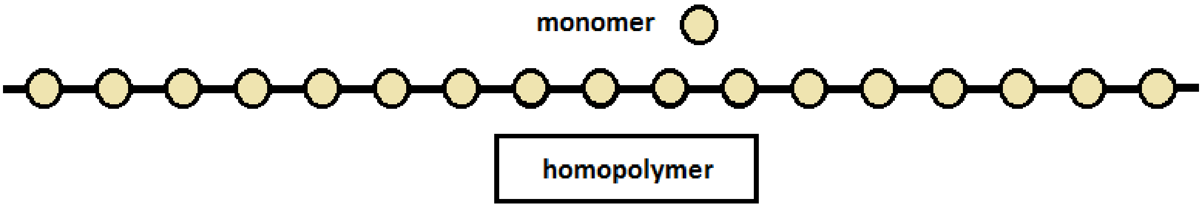


Figure 12-Structure of homopolymers

- copolymers: consisting of at least 2 different monomers that are repeated in the chain in the following ways:

    a) alternating: the monomeric units are repeated alternately

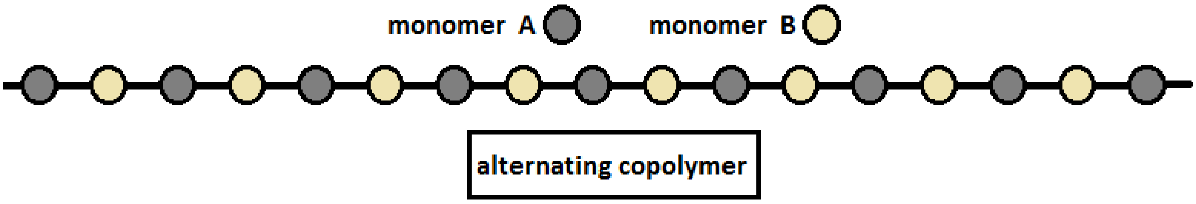


Figure 13-Structure of copolymers

    b) random: the monomeric units randomly follow each other in the chain

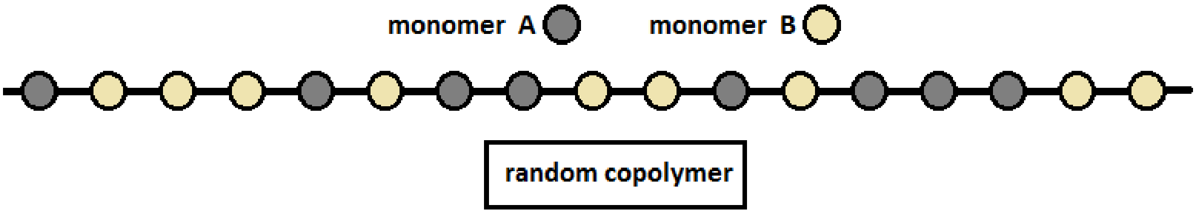


Figure 14- Structure of random polymer

c) in blocks: in the chain alternate rather long blocks consisting of a single monomer (block copolymer)

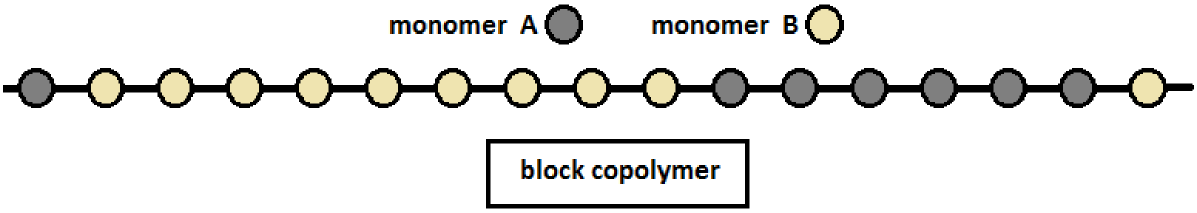


Figure 15-Structure of block copolymer

d) grafted (or stapled): in the main chain, consisting of a single monomer, a second chain is inserted laterally, constituted by the second monomer

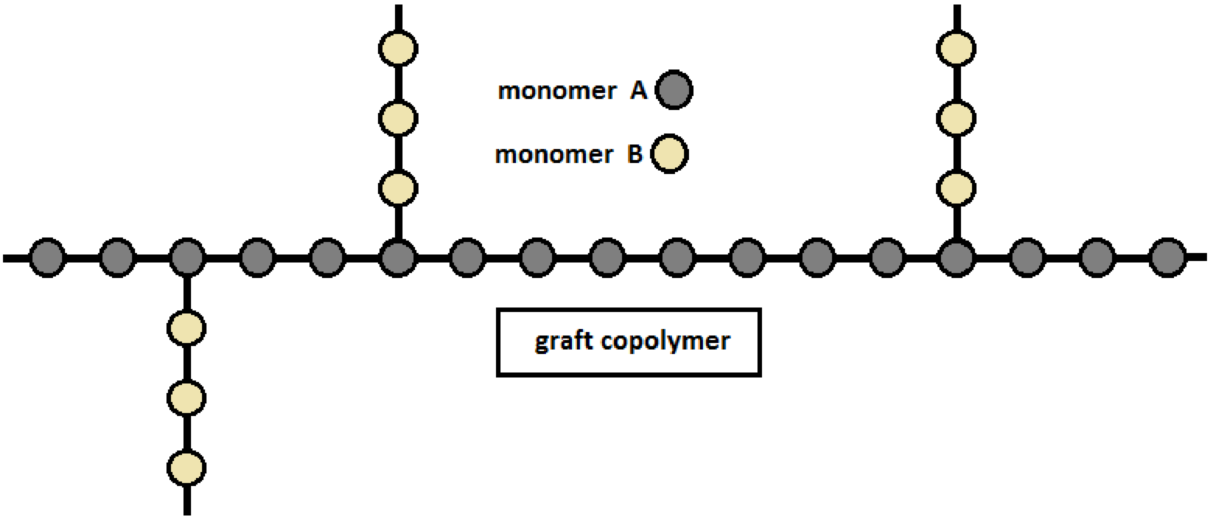


Figure 16-Structure of grafted polymer

Polymers could be classified according to the chain made of:

- linear (linear), consisting of individual linear chains
- branched (branched), consisting of a chain with lateral ramifications
- crosslinked (cross-linked), consisting of main chains connected by side chains that act as a bridge with the main chains; the cross-linked polymers in the 3 dimensions are called networks

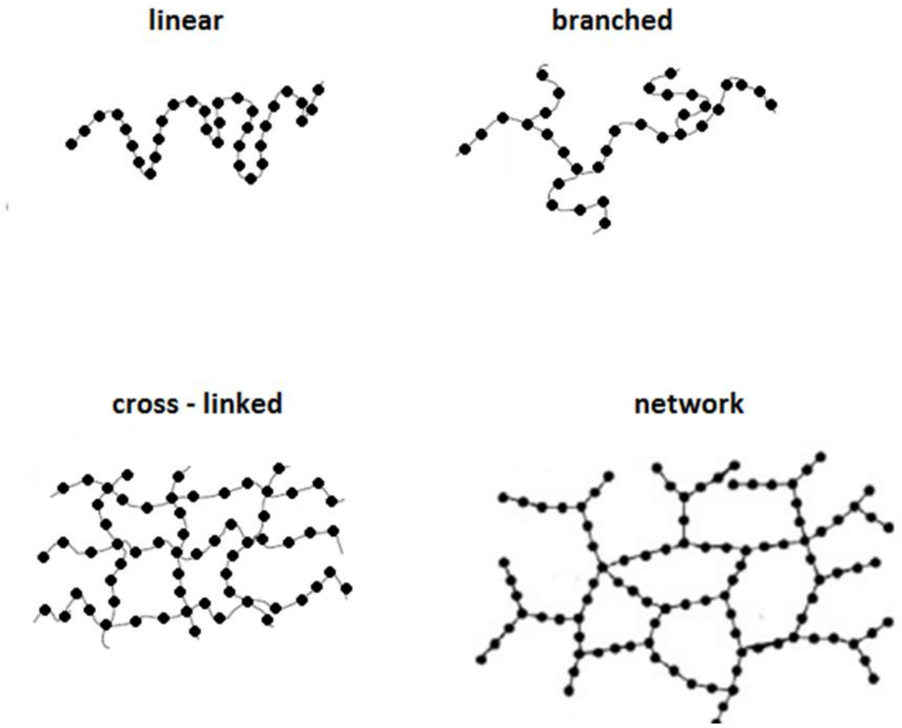


Figure 17-Types of polymer

Thermosetting polymers

Following heating or by adding specific reactants, the polymer chains can bond together forming disordered three-dimensional lattices. As a result, a predominantly amorphous state with high rigidity is achieved. The polymers thus obtained are thermosetting because the crosslinked macromolecules can no longer flow between them under heating.

The thermosetting polymers are prepared by melting only once. The subsequent heat action results in a process of breaking the bonds and carbonizing the material without passing through the melt as occurs in thermoplastic polymers. The three-dimensional structure in the final state achieved can not be changed either by external forces or, as already mentioned, by the increase in temperature.

The crosslinking therefore produces a permanent solidification, so the material becomes rigid and infusible.

The melt/solidification cycle can not be repeated several times because it is an irreversible process, unlike what happens for thermoplastic resins.

In thermosetting polymers, the mechanical properties depend on the number of transversal bonds, therefore, they range from semi-flexible products to rigid products.

The larger the lateral ramifications, the smaller the crystallinity and the greater the transparency.

So, the main advantages of thermosetting are:

- high thermal stability
- high rigidity and dimensional stability
- resistance to deformation under load
- high electrical and thermal insulation properties.

Epoxy Resins

Epoxy resins are thermosetting, infusible and highly crosslinked polymers with excellent performances thanks to their high elastic modulus, durability and resistance to thermal stress and chemical attack.

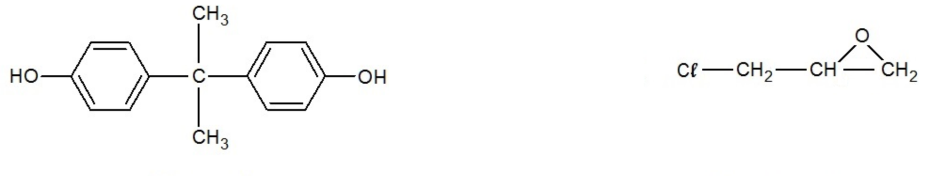
They are so named for the presence, in the precursor compounds, of the epoxide functional group.

As for all thermosetting polymers, the final polymer does not form the final polymer directly, but a low molecular weight thermoplastic prepolymer.

This prepolymer becomes liquid for heating, can be processed, and has at the ends of highly reactive groups, consisting of rings with two carbon atoms and one of oxygen (epoxy groups).

Adding a further reactive (diamine) prevents the mobility of the polymer chains and promotes the formation of chemical bonds between different chains, thus obtaining a three-dimensional lattice structure. This produces a hard and tenacious material, consisting of a single large molecule, which can no longer be transformed.

The most widespread epoxy resins are those made by the Bisphenol A and by the epichlorohydrin:



Bisphenol A Epichlorohydrin

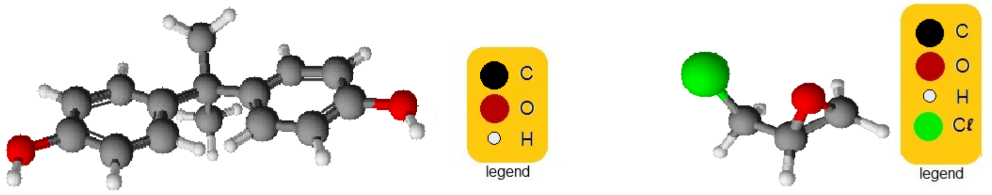


Figure 18-Reagent Structures

From the reagents (Bisphenol A and Epichloroydrin) the final polymer is not obtained directly, but a thermoplastic pre-polymer with a low molecular weight (at most it generally assumes a value of 25), which occurs in the liquid state by heating and can be processed; at the ends it has highly reactive groups, consisting of the rings with two carbon atoms and one of oxygen, the epoxy groups (Epoxide group).

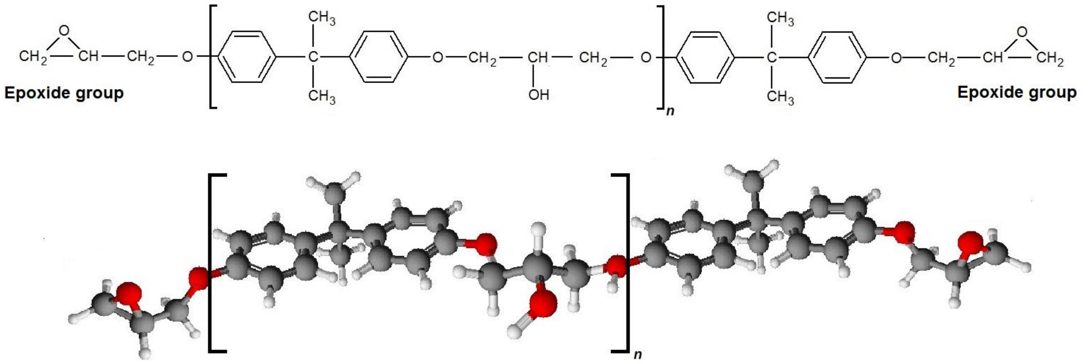


Figure 19-Prepolymer bisphenol A

To obtain the epoxy resin, a suitable hardening agent is introduced, e.g. a diamine.

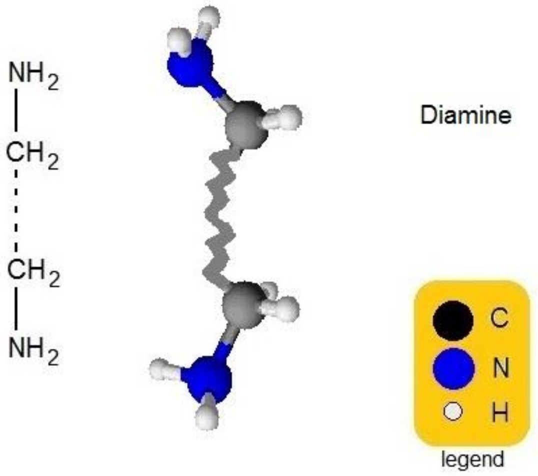


Figure 20-Diammine

From a chemical point of view the epoxy groups of the prepolymer react with the amino groups of the diamine and the thermosetting crosslinked polymer is produced: the new chemical bonds between different chains will prevent the mobility of the chains themselves and thus a three-dimensional lattice structure will be obtained and therefore a hard and tenacious material, consisting of a single large molecule, which can no longer be transformed.

The chemical process between the epoxy group of the prepolymer and the nitrogen of the diamine is illustrated in the following figure.

The nitrogen is further combined with another epoxide group and, ultimately, the thermosetting polymer is obtained through a complex crosslinking.

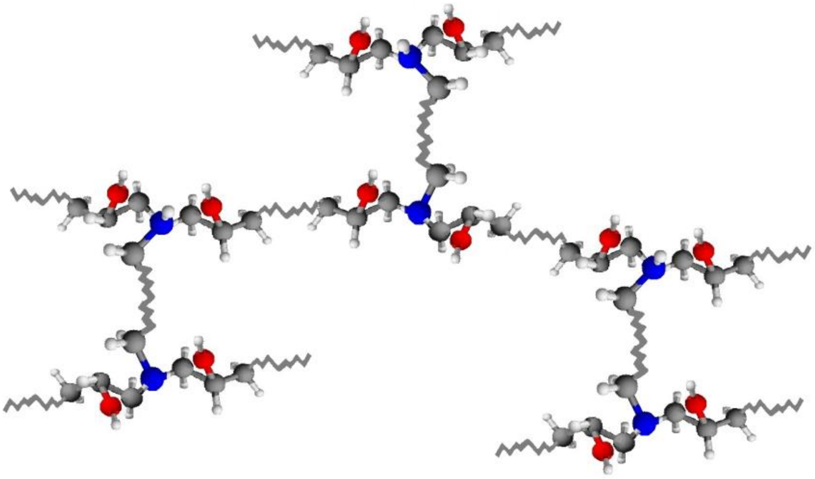


Figure 21- Reticulated resin structure

The cross-linking process transforms the medium-low molecular weight material into a solid with a theoretically infinite molecular weight. The process takes place at high temperature and for long times which give the final properties.

Epoxy resins can be formed and laminated and allow to create components made of fiber reinforced material that has better mechanical, electrical and chemical characteristics than those obtained, for example, using unsaturated polyesters. Only the price of epoxides prevents a more massive use of these materials. (Engels, 2012)

1.4.2 Carbon Fibre Composites in Automotive

Many industrial sectors have seen in the last years a huge increase in the demand for composite materials and among these, one of the most important in terms of investment is the automotive sector. Many authors (Takashi Ishikawa, 2017) focused their studies on this topic trying to explain the advantages of composites, what led to the widespread of them and the basic physics of the fibers distribution mechanism and procedures to measure fiber distribution.

A strong motivation to apply CFRP to automotive structures is due to the necessity of decrease the weights of cars which leads to less emission of CO_2 and, of course, to an increase of global efficiency of the system: a lightweight car needs less power, so less fuel. It is very important to understand what the main factors that a car must win for the motion in terms of resistance are.

According to other studies (Composite World, 2014) every reduction of 45 kg on a car can lead to an improvement of 3% on the efficiency and consequently with a less need of power many components could be reduced in terms of dimensions.

The mains hurdles to win are the cost (up to 10 times that of metal), time and recyclability. The cycle time must be comparable to that one of metals to improve composites application in the automotive sector: this is the reason by which some processes like RTM or Compression Molding are developed more than others. Some predictions say that carbon fibers cost must be less than $5/lb in order to make it viable for car making. Regarding the recyclability, instead, there is not yet the possibility to absorb all the market.

Beardmore and Johnson (Johnson, 1986) analyzed the 2 main limits on the structural viewpoint regarding the application of composites. These are durability in term of fatigue response and energy absorption. Stress-strain curves for high performances composites are essentially linear with only elastic deformation; this is in contrast with metals characterized by a high degree of plasticity. To win this kind of limitation is necessary to control the fracture process with the so-called “dissipation cone”. The main goal of the future is to try to understand the influence of the 2 limits for complex structures and loads.

Most applications of CFRP could be body, wheels, doors, bumpers, drive-shaft and all of them could bring to a reduction of 50% of the weight of a car with all steel components.

A study on the manufacturing of a one-piece drive-shaft with aluminum and carbon fiber epoxy composite has been developed by Cho *et al.* (Durk Hyun Cho, 1997). The goal is to increase the natural bending frequency, which should be higher than 6500 rpm to avoid vibrations, without changing the transmission capability, which should be larger than 3500 Nm. The natural bending frequency of 1-piece steel or aluminum longer than 1 m cannot be higher than 6500 rpm so the drive shaft is made of 2 pieces which represent a heavy body causing vibrations transmitted to the vehicle. Using carbon fiber composite, which stiffness is 4 times that one of steel, it is possible to manufacture 1-piece body.

The drive shaft was designed using aluminum, which main role is to transmit the torque, and CFRP which provide an increase of natural bending frequency. In this way, thanks to dynamic tests, it has been possible to obtain the first natural bending frequency of 9000 rpm and a torque transmission of 3550 Nm.

One other application of composites is shown by Al-Qureshi (Al-Qureshi, 2001) and it is based on automobile leaf springs. The study involved in a realization of composites springs and comparison with steel springs. It demonstrated that composites can be used for light trucks with weight saving even if in the case of automobiles, the weight reduction may not cause any technological impact.

As introduced before, one of the main constraints in the development of cars is the emission of pollutants. The ‘Euro 6/VI’ vehicle emission standard adopted by 2016 and developed with ‘Euro 6c’ and ‘Euro 6d’ which will be valid from 2019, regulated the number of pollutants with a reduction of 96% from Euro 1 limits (NO_x limit quantity is 0,170 mg/km) (A technical summary of Euro 6/VI vehicle emission standards, 2016).

It is clear that what emerges is the necessity to improve the total efficiency of cars and a contribution to this problem could be the reduction of the motion resistance reducing the weight.

Using composite material parts can lead to saving up to 50% in the weigh compared to steel, but the biggest limitation is the part cost which could be 5 times higher (Sabadka, 2015). Many developments are done in the last few years, passing from 42 €/kg to 23 in 2015 with a prediction of 14 in 2030.

Applications:

- Wheels
- Body
- Dash Panel
- Bumpers
- Monoquoque
- Drive shaft

Figure 22-CFRP in automotive

1.5 Defects

An important parameter to keep the attention on are defects in composite materials. As for the metals, defects can influence the mechanical properties like tensile strength or Young’s Modulus. For this reason, an accurate analysis is necessary to characterize parts in an acceptable way. The main reason that causes defects is the manufacturing process and, of course, the optimization of a process has as a goal the minimization of them.

Below are proposed the most commons defects in composite materials (Smith, 1968):

- Porosity (voids) refers to the presence of entrapped air or other volatile components between matrix and fibers. It is the most common defect in composites and it could be evaluated by microscope, by Archimedes test or by ultrasonic method.

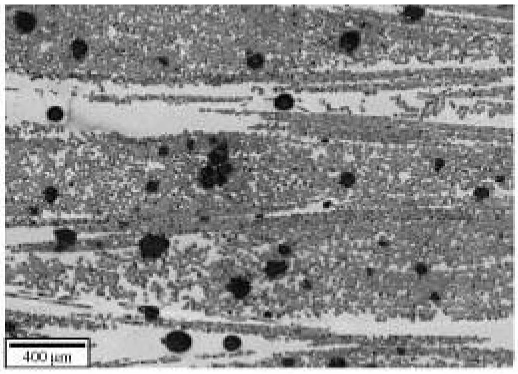


Figure 23- voids in composites (Paciornik & d'Almeida, 2010)

- Foreign bodies: refers to the presence of a substance that differs from matrix and fibers. It causes a decrease in mechanical properties.
- Incorrect fibre volume fraction: it could be caused by the excess or insufficient resin. Of course, the fiber volume fraction is not a homogeneous property in the parts so local variations will always occur.
- Bonding defects: it is very important for a composite to have good bonding between the 2 phases. Bonding defects can be caused by incorrect curing cycle and can refer to the contamination of the bonding surface.

- Fiber misalignment: refers to the variation of the angle between the fibers causing local changes in volume fraction.

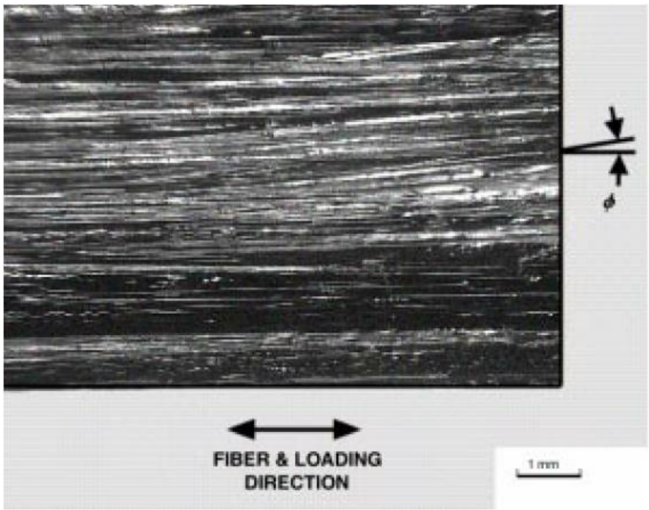


Figure 24-Fiber misalignment (Waas, 1999)

- Incompletely cured matrix: it might determine bad mechanical properties and for thermoset resin, it could cause the not solidification.
- Wavy fibers: refers to the shape of fibers in a laminate and can affect the strength of the material.

Figure 25-Wavy Fibers (Smith, 2009)

- Ply cracking. Thermally induced cracks occur with certain ply lay-ups due to differential contraction of the plies after cure.

- Delaminations: it is caused by interlaminar stresses and fibres and it caused by the fact that fibres lying do not provide reinforcement through the thickness, and so there is a separation of the adjacent layer.

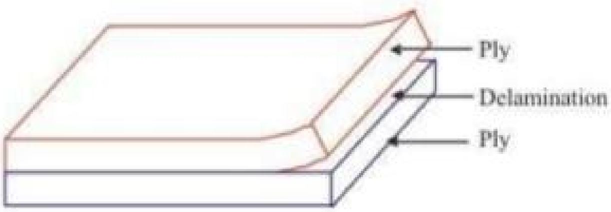


Figure 26-Delamination (SLideshare, 2019)

2 Liquid Compression Molding

Liquid Compression Molding (LCM), or Wet Compression Molding, is a process similar the more know RTM but, instead of the injection phase, the liquid resin is placed on the fabric and then the mold is closed. After that, the curing phase is necessary to obtain the final part. So, LCM can be classified as a closed mold process for polymer matrix and usually for carbon fibers.

The goal of the study is to improve a process suitable for automotive sector and in particular, suitable for high volume of production, for light weigh structures, for low expensive components and for consistent quality parts.

LCM has been developed to win one of the biggest limitations of composite parts: the high manufacturing cost.

To decrease the cost of each component it is possible to decrease the cost of the material or to develop some technologies capable to lower considerably the cycle time. Of course, to do that fast-cured resin must be used with a high level of automation. The cycle time of LCM is lower than that one of RTM because is not necessary to inject the resin, so it spreads faster, and another big advantage is a comparison with RTM is that is not necessary an injection molding screw which represents a big investment in terms of tools.

Some authors (Gardinier, 2016) described the main general features of the process and introduced its development which goes under the name “Dynamic Fluid Compression Molding”.

On the other hand, some limitations of LCM could be linked to the difficulty in spread correctly the resin with complex shapes (the pressure is much lower than HP-RTM), the percentage of the voids content could be higher since the presence of air into the cavity and the quality surface of the parts is not consistent as in other processes.

2.1 Process Steps

The Liquid Compression Moulding is made of the steps showed below:

a) The dry fabric is placed inside the open mold, prehated to the desired temperatuere.

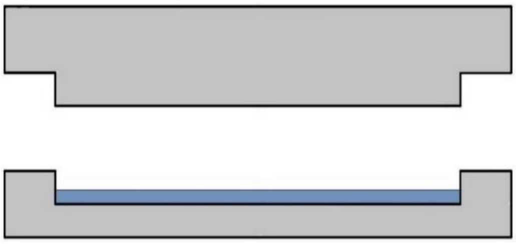


Figure 27-Step 1 LCM

b) A calculated quantity of degassed resin is placed over the fabric in the open tool.

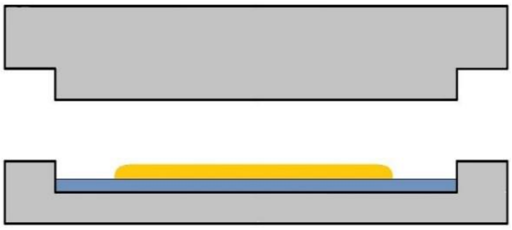


Figure 28- Step 2 LCM

c) The mold starts to close, and the resin starts to spread inside the cavity and between the fabrics. The temperature of the components inside the mould, starts to grow causing the decreasing of the resin viscosity and at the same time, even the pressure grows generating the impregnation of the resin through the fabric. An important role in this phase could be vacuum supply: it is necessary to obtain a homogenous spread of the resin inside the cavity and the fewer voids fraction possible.

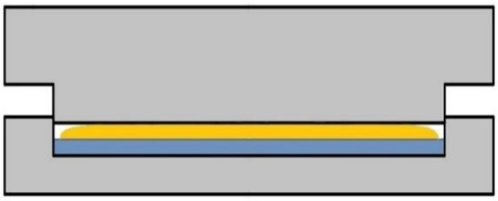


Figure 29- Step 3 LCM

d) After that the mould is closed, the plastic has to been cured. Curing cycle is necessary to improve the characteristics of the thermoset and it is achieved thanks to the heat given by the preheated mould.

Figure 30- Step 4 LCM

e) The end of the curing cycle is followed by the cooling step necessary for the consolidation of the part and the extraction.

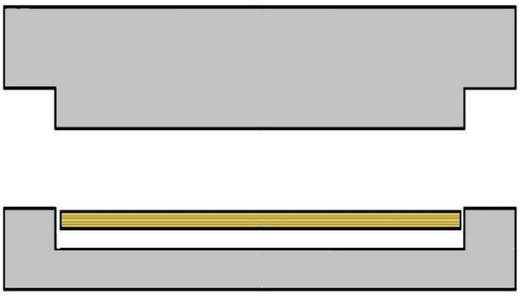


Figure 31- Step 5 LCM

The main advantages of LCM in relation to HP-RTM is that the impregnation is much more faster decreasing the cycle time. It is due to the fact that, since there is no injection gate and the resin occupies a bigger area on the fabric, the direction of impregnation is uniform in all the direction.

Here a scheme of the impregnation of the resin through the fabric:

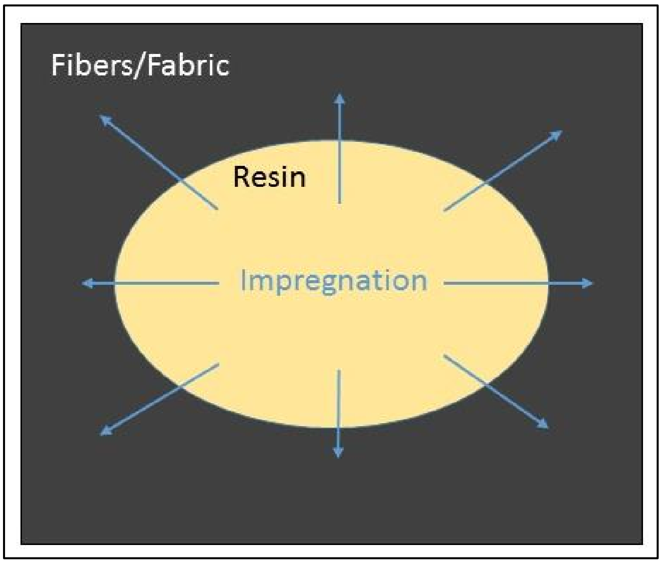


Figure 32-Impregnation of the fibers

Also, since there is no gate for the injection, the pressure during the compression phase is lower which means saving costs in terms of machines and energy.

2.2 Material Properties

The goal of the research is to improve the quality of panels made by Liquid Compression Molding. The panels are made of epoxy and carbon fabric and for a better characterization of the final part, is important to define the main properties of these 2 components.

1. <u>Fabric</u>

The fabric used as a reinforcer of the panels is a "ZOLTEK PX35-UNIDIRECTIONAL FABRICS" and in particular a "UD300". ZOLTEK PX35 are continuous carbon fibers manufactured from polyacrylonitrile (PAN) precursor. The carbon fibers have a 0º orientation and they are held together by 90º orientation glass fibers. In the picture below is possible to see the carbon fibers held together by the glass fibers (white):

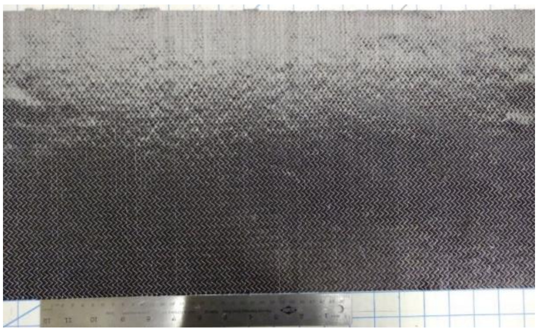


Figure 33-Fabric

These fabrics are used in many fields like wind energy, automotive, petroleum production, aviation, marine, industrial, other transportation, medical (including X-ray), sports and recreation, etc.
Main properties of the fabric are expressed in the table below:

Table 3-Properties of Fabric

Tensile Strength [MPa]	4137
Tensile Modulus [GPa]	242
Elongation	1.5 %
Electrical Resistivity [ohm-cm]	0.00155
Density [g/cc]	1.81
Fiber Diameter [µm]	7.2
Carbon Content	95 %

2. Resin

The resin used in manufacturing the panels is provided by the company Hexion.

It is a low viscosity resin designed for composite application and in particular for a good adhesion to the aramid or carbon fibers. This thermosetting polymer has to be mixed with a curing agent to obtain the solid part and with an additive to help the extraction (it acts like a mold release). Typical applications are structural automotive parts such as parts of the frame or chassis, floor panels, bulkheads monocoque structure, and exterior and visible structural parts such as roof tops, pillars, heads and deck lids.
The resin is an “EPIKOTE™ Resin TRAC 06150”, the curing agent “EPIKURE™ Curing Agent TRAC 06150” while the additive “HELOXY™ Additive TRAC 06805”.

The main properties of the resin for this study are shown in the table below:

Table 4-Properties of Resin

Viscosity at 25°C [mPa·s]	8000 - 10000
Density at 20°C [kg/l]	1.15 - 1.19

The main properties of the curing agent are shown in the table below:

Table 5-Properties of Curing Agent

Viscosity at 25°C [mPa·s]	10-20
Density at 20°C [kg/l]	0.97

And finally, the important properties of the additive agent are:

Table 6-Properties of Additive

Viscosity at 30°C [mPa·s]	750±450
Density at 20°C [kg/l]	1.01 - 1.05

The typical properties of the system after the curing cycle and without the reinforcer, so only resin+curing agent+additive, are:

Table 7-Typical properties of System 6150

TG [°C]	118 ± 2
Thermal expansion coefficient [ppm/K]	< 75
Tensile Strength [MPa]	85 ± 2
Tensile Modulus [MPa]	2900 ± 100
Elongation at break	6 - 8 %
Density at 23°C [kg/l]	1.151 – 1.155

2.3 Setting the Process

Some pre-setting operations have been considered before starting to manufacture components by the Liquid Compression Molding. The tree main components required to go on with the process are the mould, the fabric and the resin.

2.3.1 The Mould

The mould is critical for placing the fibers, the resin and then forming the part. It is a "Plaque Mold" by Laval International and it is composed of P20 steel, commonly used in the manufacturing of plastic parts. The mould is provided with one cavity of dimension 12*12 inches and thickness, when fully closed, of 1.7 mm. No ejector system is included in the tool.

The picture below shows the CAD of the mould:

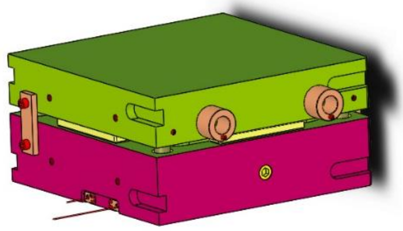


Figure 35-Mould

The most interesting part to manufacture components is, of course, the cavity. As said before it is parallelepiped with a square section. The pictures below of the male and female of the tool can explain better the shape of it:

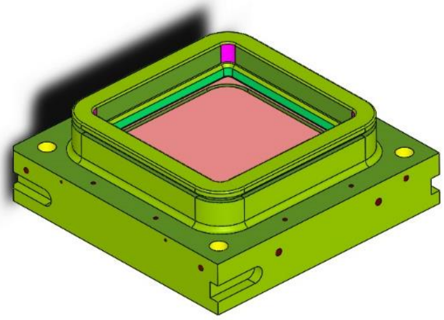


Figure 36-Female mould

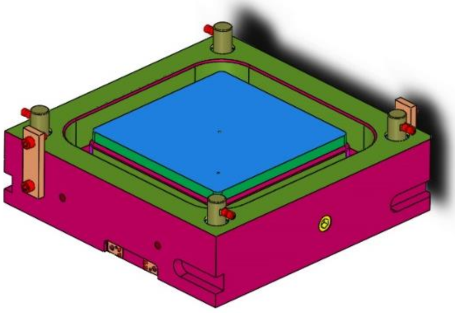


Figure 37-Male mould

It is important to analyze a particular of the female part. On the sides of the finished surface, there is a grove made to contain a seal useful to hold the resin inside of the cavity and not letting move the fabric during the compression phase.

Since it is a floating mould, the only parameter or degree of freedom between the dimensions of the part that can be managed during processing is the thickness. A section of the female part is provided to show the groove for the seal:

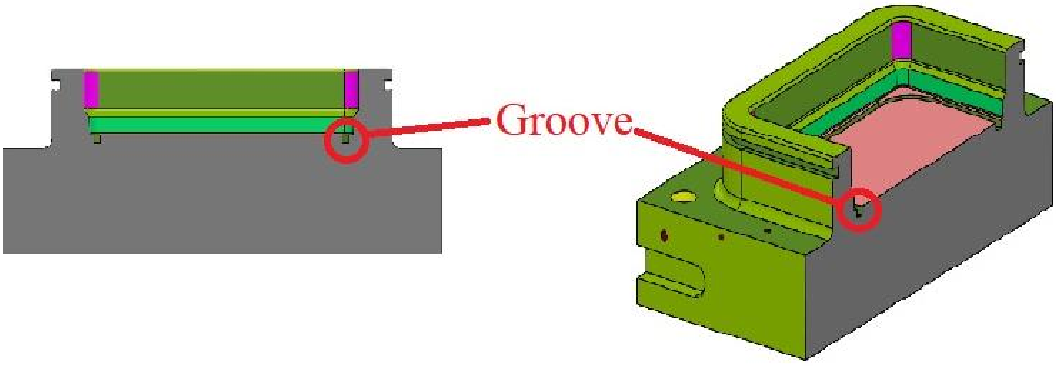


Figure 38-Female mould section

In order to reach good results in term of consolidation of the resin the fabric and the global quality of the parts, 3 shapes of seal have been used during the process. These are named as a circle, square and rectangular. The circle one has a circular section with a diameter of 8 mm; the square section is $8 \cdot 8$ mm^2, while, the rectangular is $8 \cdot 10$ mm^2. These different cross sections of seals are represented in the picture below:

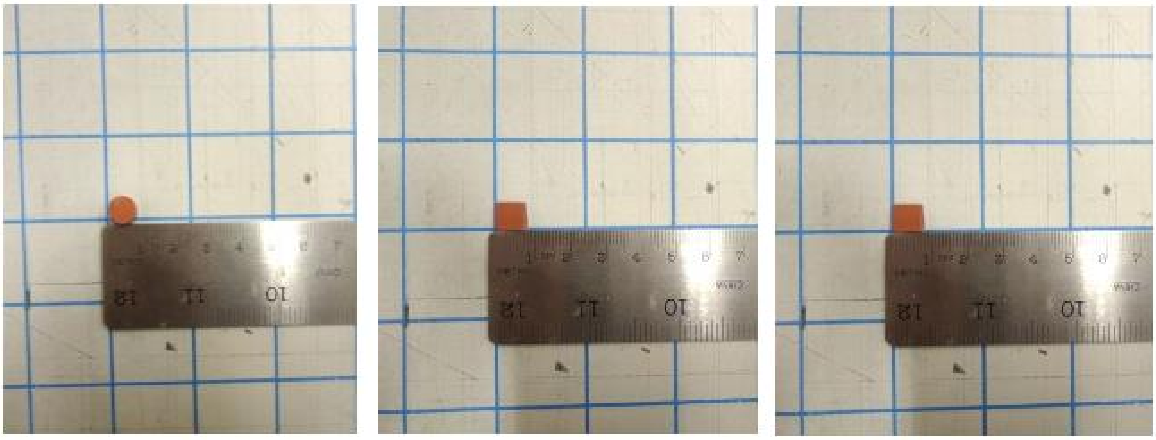


Figure 39-Different Seals sections

To process properly, the mould needs to reach 120°C and be able to apply pressure to the part.

For this reason, it has been mounted on a Whabash Hydraulic press, in particular, the following model G100H-24-CPX:

Figure 40-Mould on the press

After that, has been possible to apply the seal in the female:

Figure 41-Mould without and with the seal

2.3.2 Cutting the Fabric

The fabrics are provided wound on a big roll, so an operation of cutting according to the desired dimension of the panel is required.

Figure 42-Cutting of the Fabric

Obviously, the dimension of the fabric and of the panels is determined by the dimension of the cavity of the mould. The fabrics are cut in a square of 12 inches by 12 inches ($304 \cdot 304$ mm^2). It is important to observe the difference between the 2 faces of the fabric; this difference is due to the disposition of the glass fiber (white fibers) which are important to hold on the carbon fibers (black fibers). The pictures below show the difference between the 2 faces of the same layer of fabric:

Figure 43-Upper face of the Fabric

Figure 44- Lower face of the fabric

It could be an important parameter to analyze during the manufacturing step.

Since the mould is provided with no ejector pin, to easily extract the panel from the mould, a corner of the fabric has been cut. This corner is placed in the top right side of the fabric and it is an isosceles triangle with a length of the sided of 2 inches.

The picture below explains better the corner cut to help in the extraction of the panel:

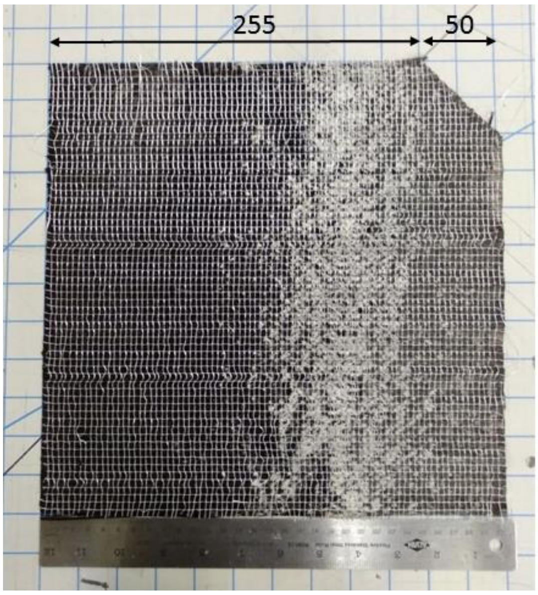


Figure 45-Corner cut of the fabric

2.3.3 Quantity of the resin

The resin is provided in the pail, so the quantity for each part must be weighted or measured by the volume. As said before, the system is a 6150 provided by the Hexion company and it is made of the resin, the curing agent and the additive.

The datasheet of this system shows the ratio on weight for each component:

$$resin: curing\ agent: additive = 100: 24: 1{,}5$$

Mixing exactly these 3 components is essential for an optimal result in terms of quality of the panels. The operation of mixing the element has been done in two main ways: manually and thanks to the use of an automatic metering unit, the “Super E”. The quantity of the resin to use for each panel is calculated considering the goal to be achieved: panel with a dimension of 12·12 inches (304.8·304.8 mm^2) with a fibre volume fraction of 55%.

So, the volume of the resin should the 45% of the volume of the total panel, and keeping in mind that to reach that goal the thickness should be of 2.5mm, the total quantity of resin is 104.52 cc.

Table 8-Properties of the panel

Area of panel [mm^2]	$9.29 \cdot 10^4$
Thickness [mm]	2.5
Volume of panel [mm^3]	$2.01 \cdot 10^5$
Fibre Volume Ratio	55%
The volume of Resin [mm^3]	$1.05 \cdot 10^5$

So the volume of resin is equal to 104.52 cc.

Considering the density of the element of the 6150 system, it is possible to calculate the ratio based on the volume: 10^5

Table 9-Ratio of the elements

	Weight [g]	Density [kg/L]	Volume [cc]
Resin	100	1.15 - 1.19	85.47
Curing Agent	24	0.97	24.74
Additive	1-2	1.01 - 1.05	1.46

So, the ratio based on the volume is:

$$resin: curing\ agent: additive = 100: 29: 1.7$$

For each panel the quantity of each component is:

Table 10-Quantities of the elements

	Weight [g]	Volume [cc]
Resin	94.9	81.1
Curing Agent	21.4	22.1
Additive	1.4	1.4

The manual operation has been done weighing each component in a suitable container and mixing all of them together with the use of a rod of material that does not react with the elements.

Considering the material remaining in the container when the resin is placed on the fabric, a corrective factor equal to 10% more has been used to solve this problem.

So, the final quantity for each panel, in the case of manual mixing, is:

Table 11-Weight of the elements for manual mixing

	Resin	Curing Agent	Additive
Weight [g]	104.4	23.5	1.5

2.3.3.1 The Metering Unit

As said before, an automatic machine to mix the elements of the 6150 system has been used to manufacture some panels. The machine is called “Super E” provided by the company “Micheal Engineering”. Before starting to operate the unit, a “Standard Operating Procedure” has been done to understand how the machine works and the hypothetical risks connected to it. The SOP is attached in the appendix A and below is explained the main principles of the machine.

The main components of the machine are: a tank for the resin and for the curing agent, monitor to manage the parameters (E-stop touchscreen), trigger or pedal to dispense the material and the system hose-gun-static mixer to mix and spread the components.

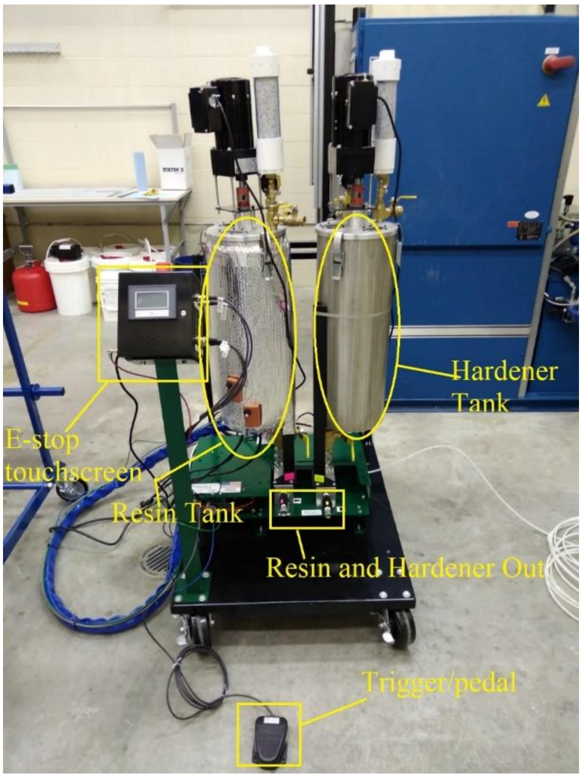


Figure 46-Metering Unit

It is useful to shortly explain how it works: at the base of each tank, there is a piston which, every time that is pushed enters in its cylinder and the material from that pump begins dispensing. The pistons are connected to a pivot arm which is pulled and pushed by the air cylinder and it is constrained to a pivot.

Also, the metering is suitable to degas the materials before dispensing, decreasing the presence of voids in the results.

Some heaters on the resin tanks, furthermore, provided to decrease the viscosity of the resin for an easy process.

The bellowing scheme shows the main characteristic of the machine:

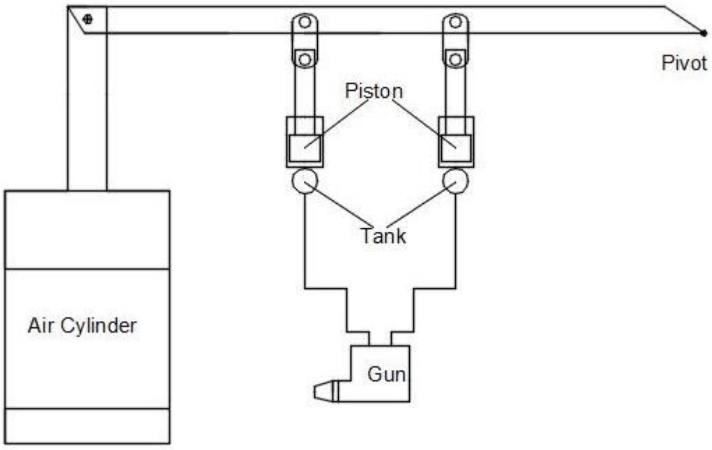


Figure 47-Scheme of the metering unit

Since it is a new machine for the process, some pre-setting operations have been done before using it.

-The tanks are provided with a vacuum controller on the lids, so it is necessary to check if it is possible to hold a vacuum of 27-29 Hg for a short period of time (few minutes).

-It is fundamental to avoid the presence of air in all the components of the machine. For this reason, the hoses must be stretched, and a few quantities of materials must be used to pull out all the air.

-Considering the ratio to use with the 6150 epoxy, the ratio by which the machine was delivered has to be changed. It has been done sliding the right-side pump (hardener side) and placing it in order to respect the instructions provided by the seller. Moving the hardener tank closer to the resin one increase the ratio up to 27/100.

Once set the ratio and checked it, the tanks have been filled with the use of a vacuum source.

The lid is provided with different valves helpful for gilling and degassing:

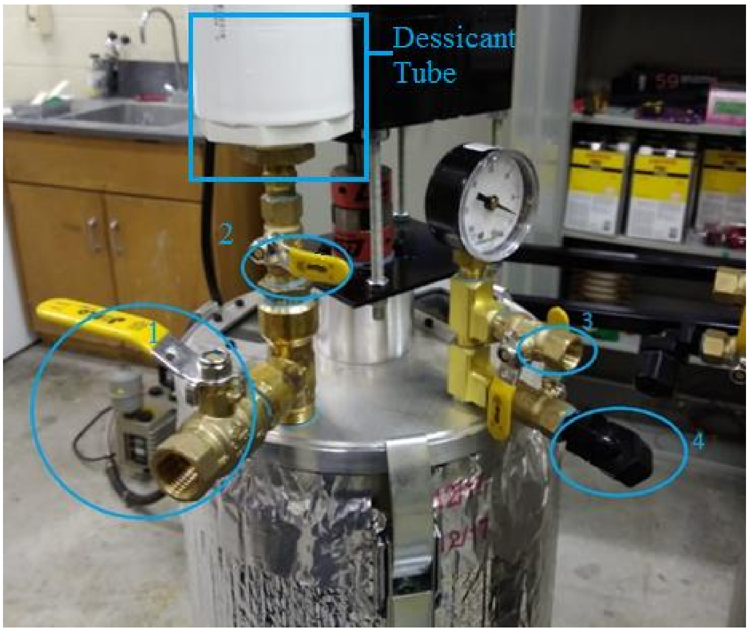


Figure 48-Valves on the lid

The role of each valve (number 1 to 4) is 1-Material intake for degassing; 2-Clean and dry air to return atmospheric pressure after degassing the material; 3-Nitrogen intake; 4-Pull the vacuum. So the procedure to fill the tank is: valve 1 is connected to a hose which is acting like a large straw that is in the pail of material sitting on the floor. A vacuum source is connected to valve 1. So, opening the valve 4 and starting to pull let the material fill in the tank, as shown in the picture below:

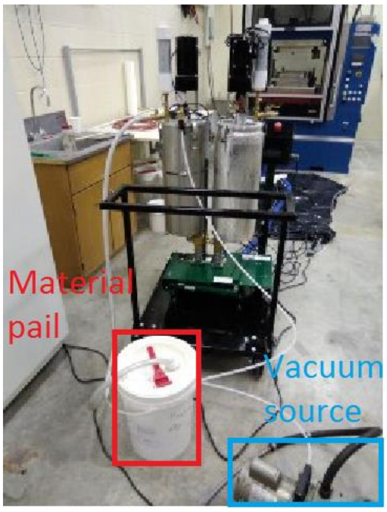


Figure 49- Filling the tank

After that, the materials have been degassed pulling the vacuum through the valve 4. During degassing the material rises and foams:

Figure 50-Rising and foam of the resin

Figure 51-Degassing

Once completed all of this operation and having connected the gun to the hoses and the static mixer to the gun is possible to dispense material.

Figure 52-Gun with static mixer

2.4 Manufacturing procedure

The manufacturing procedure is focused on the steps to realize panel with a volume fraction of 55%. The dimensions of the panels are provided by the dimension of the cavity, so $30 \cdot 30$ cm^2 and for that fibre fraction, the thickness is around 2.5 mm as suggested by previous studies with CFRP.

The process has been developed with 3 main steps: manual mixing without degassing, use of the metering unit with degas materials and finally, using of metering unit and the vacuum source during the closure of the mould.

During these steps, the "degree of freedom" of the process have been:

- Pressure;
- The temperature of the upper and lower cavity;
- The quantity of resin;
- Type of seal in the female part of the mould;
- The timing of allying the vacuum to the mould.

The datasheet of the resin system 6150 shows a curing cycle of 300 s with a temperature of 120ºC. The timing to respect this cycle is an easy parameter, but the temperature is more critical.

The mould is made of upper and lower half-mould which could be heated with 2 different temperatures.

Some attempts have been done to avoid different thermal expansion of the 2 parts which could damage the cavity. Also, another critical factor is that the heat sources are the plates of the press, so there will be a waste of energy, and of temperature, between the platen and cavity side of the mold. For this reason, the lower platen has been set with a temperature of 135ºC which matches around 120ºC in the cavity, while the upper of 115ºC which matches around 110ºC.

Even if the temperature of the upper part is lower than 120ºC, this set has been proved to be most safe not to damage the mould.

Regarding the pressure, previous studies on this kind of process show a range of pressure between 20 to 30 bar. Since the press has been set with a value of force (tons), a conversion from bar to tons according to the area of the panel is required. The quantity of resin and the type of seals have been discussed previously in paragraph 2.3.3 and 2.3.1 respectively. Some attempts have been done to understand the influence of these parameters on the final results. The timing of applying the vacuum to the mould is another critical parameter. The goal is to help to spread the resin homogeneously and pull out from the air which is in the cavity and between the tows of the fabric. The expectations of the vacuum are those to have less void content in the panels and so, with the same quantity of resin a lower thickness.

The main important step to manufacture the panels are:

1. Insert the seal in the groove of the mould;
2. Apply the mould interface release to help with the extraction of the final part;
3. Preheat the mould since the upper reaches 110 ºC while the lower is about 120ºC (at least 4 hours);
4. Place the fabric in the cavity;

Figure 53-Fabric in the mould

5. Place the resin with the right shot size;
6. Close the tool and cure for 5 min;
7. Extract the component.

Figure 54-Extraction of the panel

During the laboratory activity, many attempts have been done to try to understand the effect of the different parameters.

First, to figure out how the resin spreads into the tool under the effect of the pressure, 3 attempts with manual mixing and with growing shot sizes have been done.

The growing of the shot size (from 50% to 100% of the calculated quantity) was followed by the growing of the pressure from 10 bars to 20 bars and all of those were made with the circle seal.

Once established that the calculated amount of resin was enough to manufacture panels with goo and homogeneous impregnation, 4 more attempts have been manufactured with a manual mixing, circle seal, same shot size but varying the pressure from 15 to 30 bars with steps of 5 bars.

What emerged was that the measured thickness with a micrometre was quite consistent not feeling the effect of the pressure and was around 2.3 mm.

Once having understood the general influence of those parameters, 2 last attempts using the metering unit and with the circle seal have been manufactured with shot size up to 120% with no change on the thickness of the panels: increasing the shot size brings to an increase of the flush out of the cavity.

The main data of the first 9 panels are reported in the table below:

Table 12-Panels with circle seal

Number	Shot Size [%]	Pressure [bar]	Thickness [mm]
1	50	10	2.32
2	80	10	2.31
3	100	10	2.35
4	100	15	2.36
5	100	20	2.34
6	100	25	2.32
7	100	30	2.31
8	110	30	2.35
9	120	30	2.38

As results of the first set of panels, the main parameter that determines the thickness of the panels is the seal.

An important effect analyzed after the first 7 panels was a little deformation after the cooling phase. In the first 7 panels the fabrics have been overlapped all in the same sense not having any symmetry which means that every upper face of the fabric was in contact with previous upper face for all 8 layers; all next panels, instead, have been manufacturing overlapping 4 layers in a sense and the other 4 in a symmetric way.

The result of the deformation and of the resolution of the problem can be seen in the pictures below:

Figure 46-Deformation of the panel

Figure47-Panel with symmetric layers

The next step has been to use the rectangular seal to help to hold more resin inside the tool to increase the thickness of the part. With the "rectangular", 5 panels have been manufactured acting on the shot size and seeing the effect of the pressure. Since with 25 bars the surface quality, so the impregnation of the fibres, was not good, only 1 attempt has been done with 25 while all the others with 30 bars.

The results and data of these 5 panels are shown in the table below:

Table 13-Panels with the rectangular seal

Number	Shot Size [%]	Pressure [bar]	Thickness [mm]
10	100	30	3.08
11	120	30	3.12
12	135	30	3.53
15	80	30	3.21
16	100	25	3.61

During the extraction of the panels by the tool, it was possible to see no flush outside the seal which means that all the resin placed on the top of the fabric, was inside the final panel. This explains the fact that increasing the quantity of resin increases the thickness. Since the thickness was to high for the goal to reach (2.5 mm), another seal, the square one, was used to manufacture more panels. As in the most known injection molding for plastic components, the flush is an important signal of enough quantity of resin for that part and a good impregnation of the fibres.

The square seal is 2 mm lower that the previous one, so theoretically should have an effect between the rectangular and the circle.

Four panels have been manufacturing starting to hold the same pressure (30 bars) and other conditions of the first attempts. Panel number 16 was made with a pressure of 25 bars, and since the quality was lower than those with 30 bars, the best level of pressure found to manufacture was 30 bars. The results of this set of panels are shown in the table below:

Table 14-Panels with a square seal

Number	Shot Size [%]	Pressure [bar]	Thickness [mm]
13	100	30	2.53
14	115	30	2.54
17	100	30	2.52
18	100	25	2.58

Panel number 17 was made to confirm the properties of number 13.

The picture below shows the result of panel number 17 extracted by the mould in which is possible to see the mark of the flush:

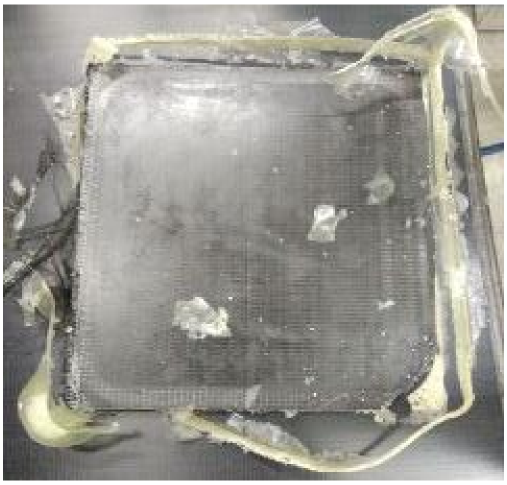


Figure 55-Panel extracted with flush

An important result is the fact that increasing the quantity of resin, bring to increase only the flush of the panel and no the thickness. The conditions of panels number 13 and 17 were considered sufficiently good to proceed to apply the vacuum supply not altering the process parameters.

So, the final results are:

Table 15- Final process parameters

T lower plate [ºC]	T higher plate [ºC]	P [bar]	t [sec]	Shot Size [%]	Seal
135	115	30	300	100	square

2.4.1 Vacuum Supply

The idea of introducing the vacuum support during processing is due to the possibility to pull out the air which is inside the mould, decreasing the content of air in the panels so decreasing the void content. It also could be a help to the resin to spreads in a homogeneous way between the fabric.

To do that is necessary to apply a negative pressure with a pump which must be connected to the mould thanks a connector.

What is dangerous is the possibility to pull out the air but also the resin before it starts to solidify. For this reason, a catch pot has been introduced between the mould and the pump in such a way that if the resin has to be sucked from the mould, it will end up in the catch pot as shown in the adjacent picture.

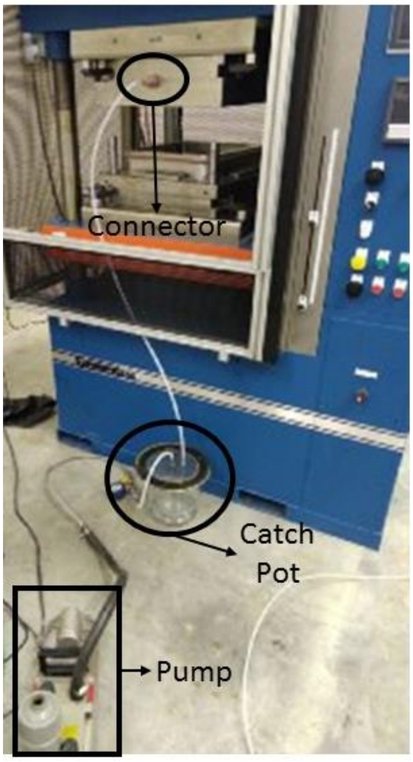


Figure 56-Vacuum supply system

The system provided should act pulling out the air from the cavity one the external seal of the female part engages the male part.

Figure 57-External Seal for vacuum

It is possible to manage the pressure regulating a ball valve between the pump and the catch pot but the only consistent level of pressure during all the process was found to be 50 bar (it is possible to control the level of pressure by a gauge on the back of the mould). Three timing level of applying the vacuum has been tested: 20, 30 and 60 seconds.

So, the panels manufactured using the vacuum supply have these parameters:

Table 16-Panels manufactured with vacuum supply

Number	Shot Size [%]	Pressure [bar]	Thickness [mm]	Vacuum pressure [mbar]	The timing of applying the vacuum [s]
20	100	30	2.48	50	20
23	100	30	2.42	50	30
24	100	30	2.56	50	40
26	100	30	2.48	50	60

One negative aspect of pulling a vacuum with high pressure or for too much time could be the risk of having air bubbles of the resin. According to that must be considered that the viscosity of the 6150 system decrease from about 1200 mPa·s at 25ºC to about 13 mPa·s at 100ºC.

2.4.2 Treating the cavity surface

As said before, the mould used with the LCM process is composed of P20 steel. It requires some treating before and after processing not to damage its surfaces and provide consistent results during the time.

Three main substances have been used for this system:

- “Loktite Frekote PMC”;
- “Loktite Frekote 770-NC”;
- “Loktite Frekote B-15”.

The substance under the name PMC is used as a solvent cleaner to remove the impurities on the surfaces. It must be applied every time after processing, after the tool is cold, to avoid any problems in the next working day.

The B-15 is a mold sealer which is useful to preserve the properties of the mold for a long time. It must be applied once every 2 months and provides an excellent base coat enhancing the release advantages offered. It must be applied a minimum of two coats, allowing 30 minutes between coats and the final coat will cure within 24 hours at 23°C

Finally, the 770-NC is also named mold interface release and has the role of helping the extraction of components. It can be applied to mold surfaces at room temperature up to 60°C by spraying. It must be applied 2 to 3 base coats allowing 5 to 10 minutes between coats for solvent evaporation.

To proceed in applying those substances, since they are dangerous and toxic, protective mask, safety glass and suitable safety gloves must be worn.

3. Microscope Analysis

In this section are presented the results of an analysis by microscope of the panels made by the different conditions. Obviously, before being analyzed, to obtain the samples is necessary to cut the panel.

It is important to understand that the "quality" region of each panel is that one inside the seal mark, so for this reason, for the side samples have been cut with a distance of about 10 mm from the mark (yellow area). Also, for each panel, 3 samples have been analyzed. The following scheme of cutting the panel is shown below:

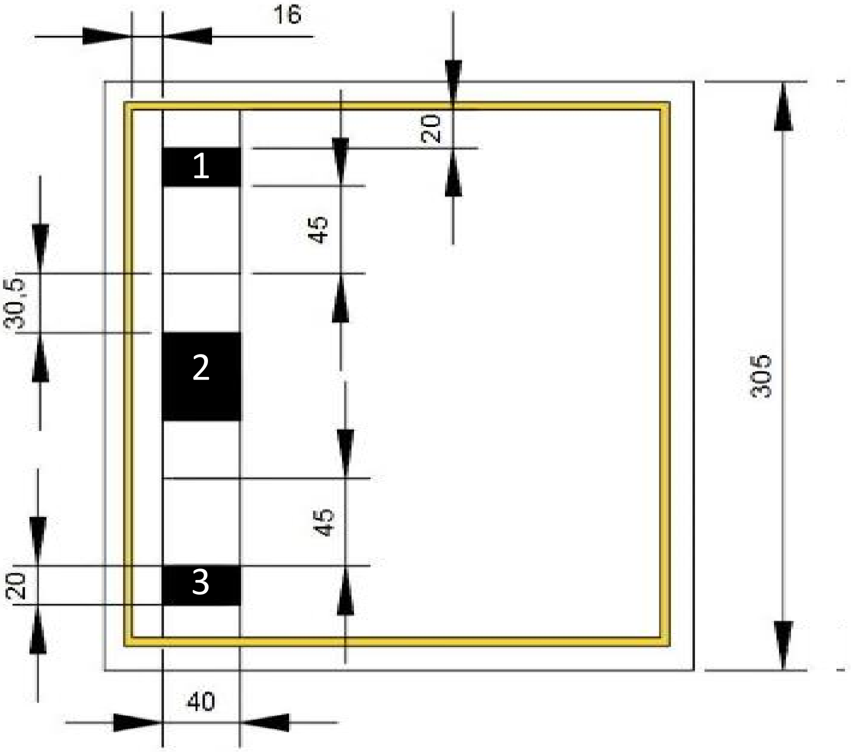


Figure 58-Scheme of cutting the panels

Where in black are highlighted the samples taken from the panel and in yellow the mark of the panel by the seal. All the quotes are expressed in mm.

The samples considered are numbered 1, 2 and 3.

Below a picture of the operation of cutting the panels:

Figure 59-Cutting the panels

After being cut, the samples had to be polished to be analyzed by microscope. The goal is to have a surface of the sample as smooth as possible. The samples have been polished using a "Forcipol Microstar 2000" using 3 grind papers with 180, 320, 600 and 1200 grit and, as the last step, a microid diamond compound. The polishing operation of a sample is shown in the picture below:

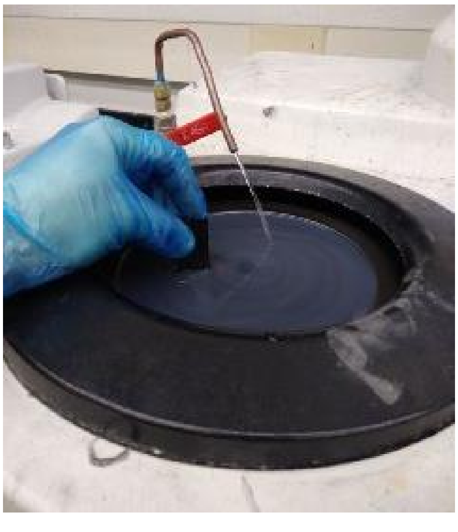


Figure 60-Polishing the samples

Once obtained the samples from the panels, they have been analyzed by microscope (KEYENCE VHX) to see the main direction of the fibers and the consistence of the quality.

Figure 61-Microscope for the analysis

The first group of panels made with the use of the circle seal, were characterized by the following results:

- ✓ The pressure does not influence the thickness of the parts: it means that increasing the pressure from 20 to 30 bars leads to similar parts,
- ✓ The shot size does not influence the thickness of the panels: having more resin on the top of the fabric before the compression phase leads to more flush at the end of the process;
- ✓ The general quality and the impregnation of the resin through the fabric is quite good and consistent but the final thickness is to low.

The pictures below, taken from the cross section to the fibers and the parallel section along the fibers, shown the presence of some general defects but at the same time homogeneous quality and parallel direction of the fibers.

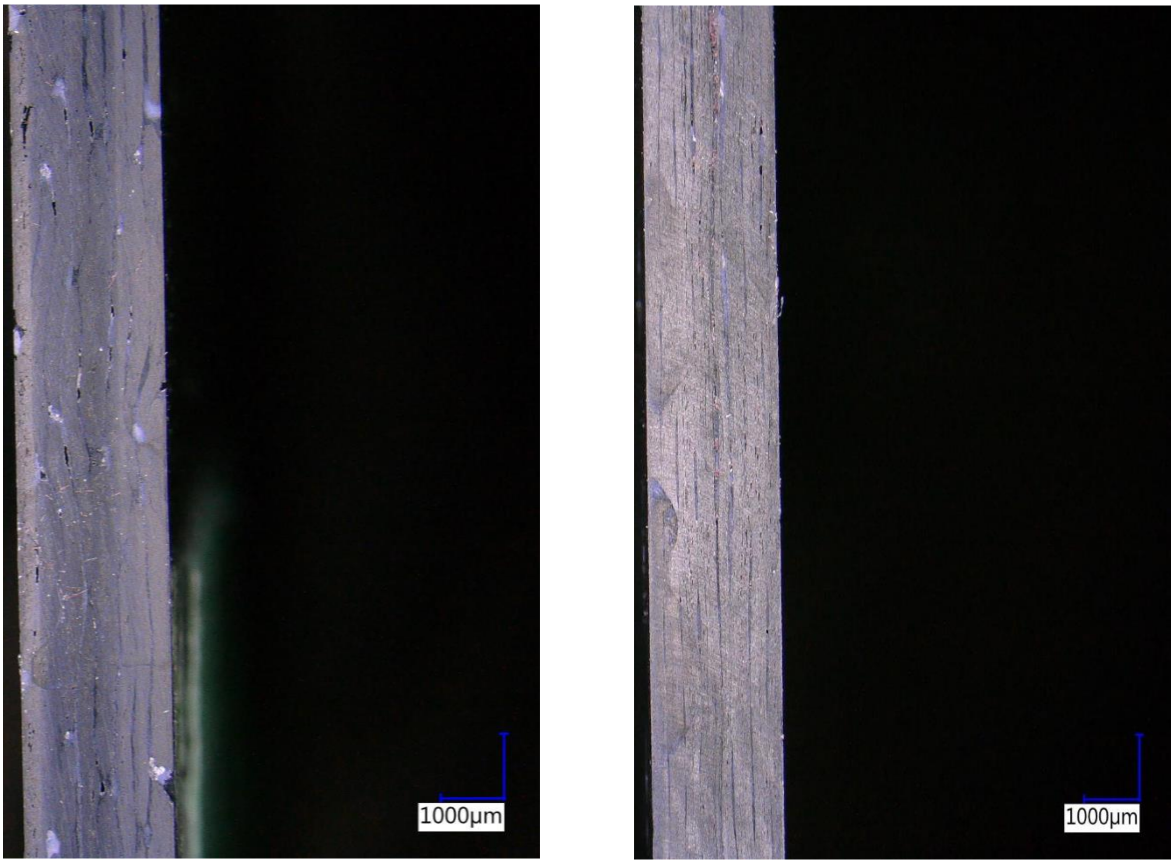


Figure 62-Cross section and parallel section by microscope of samples with circle seal

The second group of panels, manufactured with the rectangular seal, shown the following results:

- ✓ The pressure influences the superficial quality generating a better impregnation with higher level but has no effects on the thickness;
- ✓ The Shot size influences the thickness since all the resin kept on the top of the fabric is kept inside the region of the seal and for the same reason the impregnation is very bad in terms of quality;
- ✓ The final thickness of the parts was to high according to the goal to reach.

The pictures below, taken from the cross section to the fibers and the parallel section along the fibers, shown the presence of big defects through the tows and a big level of misalignment of the fibers which do not follow the theoretical direction as in the previous parts.

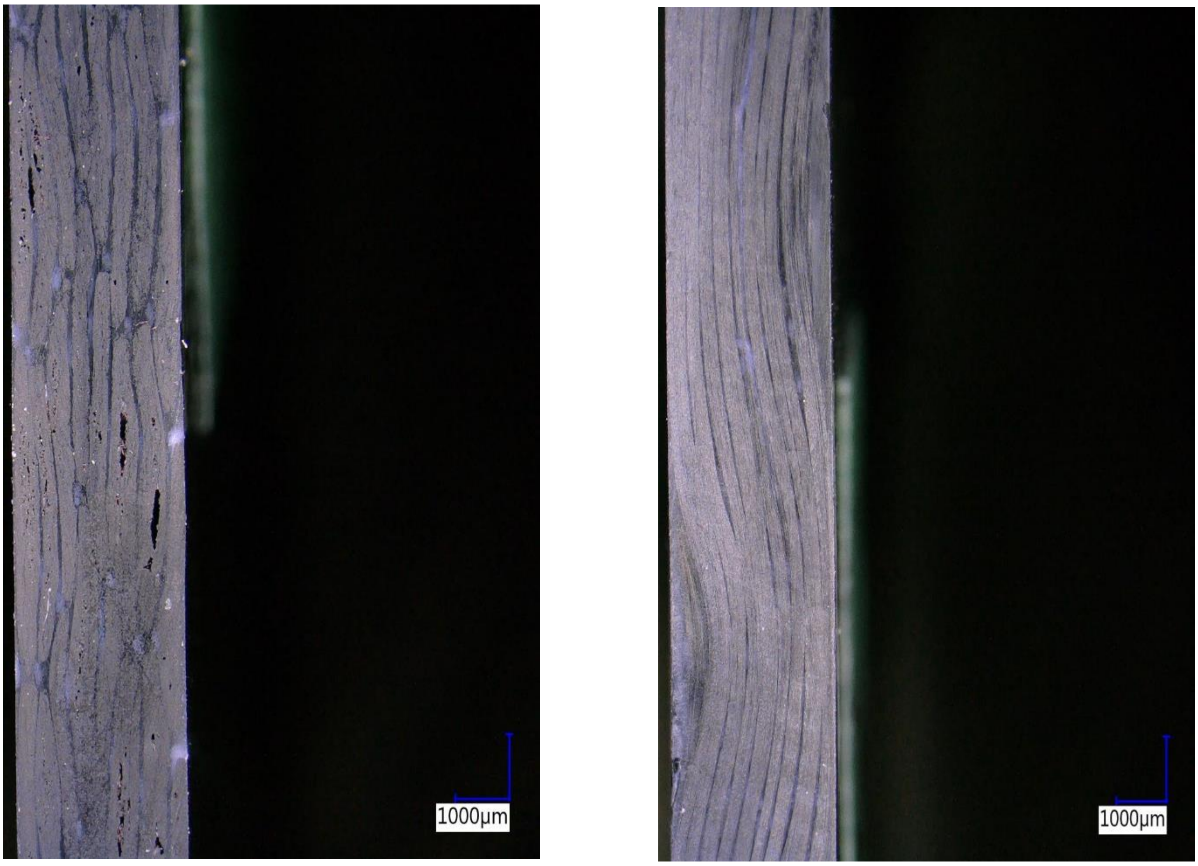


Figure 63-Cross section and parallel section by microscope of samples with rectangular seal

The last group of panels, made using the square seal, generated the following results:

- ✓ The pressure influences the superficial quality and as in the previous cases not the thickness;
- ✓ The shot size has the same role of the case with the circle seal: having more resin on the top of the fabric before the compression phase leads to more flush at the end of the process;
- ✓ The final thickness is considered acceptable for the goal established.

The pictures below, taken from the cross section to the fibers and the parallel section along the fibers, shown the presence of very few defects through the tows compared to the previous cases and a good level of alignment of the fibers which follow the theoretical direction.

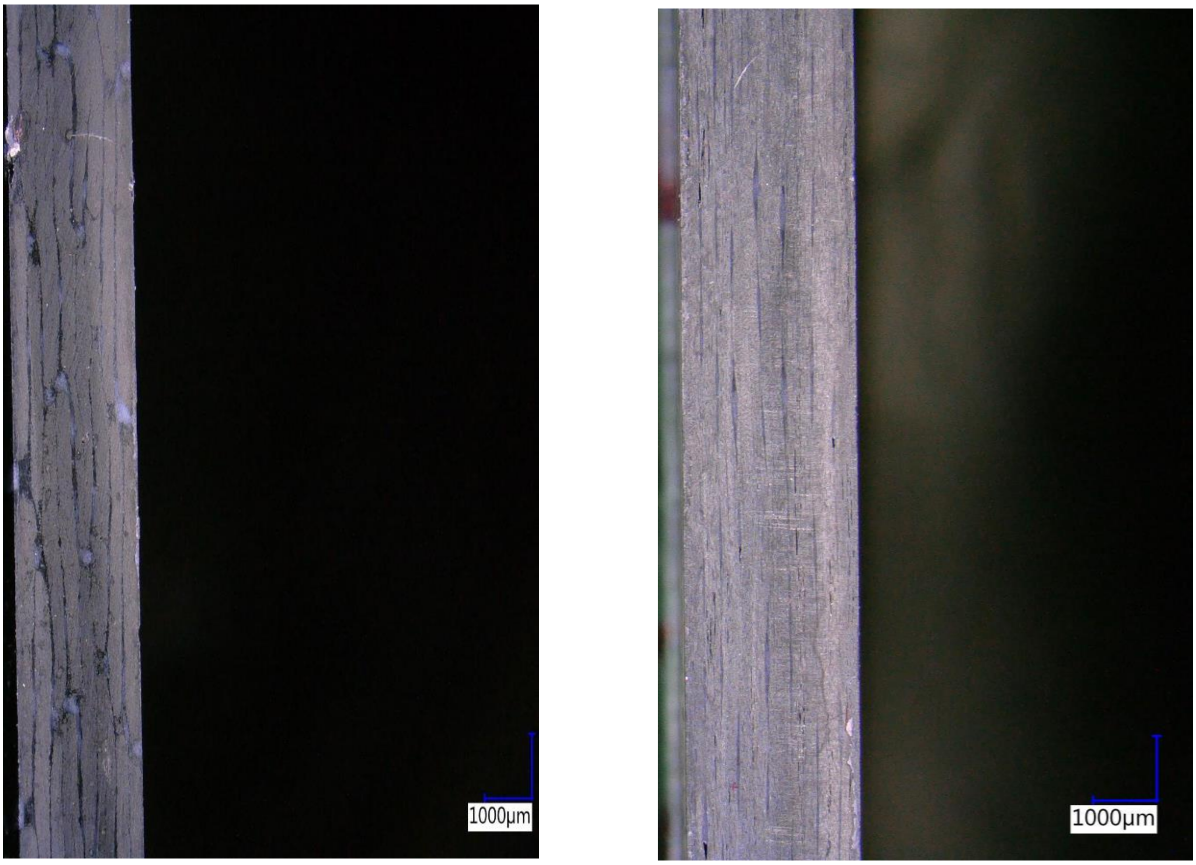


Figure 64-Cross section and parallel section by microscope of samples with square seal

4. Test procedure

4.1 Void Content Determination

The void content in composites materials is a crucial factor: it can affect some mechanical properties. High volume content brings to a lower fatigue resistance, greater susceptibility to water penetration, Youngs modulus and strength, transverse tensile modulus and strength and also shear properties. According to that, the determination void content is very important for the quality of the parts.

Many authors (P.-O. Hagstrand, 2004) found the variation in the percentage of some of those properties linked to the variation of voids, like:

•The flexural modulus and strength can decrease up to 1.5% for each 1% of voids

•The beam stiffness EI can increase up to 2 % for each 1 % of voids content.

The content is influenced mostly by the entrapped air during the process of impregnation of the fibres and by the air content in the resin. Obviously, to prevent it, some operations like degassing of resin, vacuuming of the mould, and variations of curing parameters could be done (R Olivier, 1994).

The determination of void content has been done with the ASTM-D2734 standard.

To proceed with the application of the method, the following tools are required:

- micrometre capable of reading 0.001 mm;
- caliber capable of reading the length of the specimen with 0.1% accuracy;
- weight scale capable of reading to the nearest 0.0001 g.

It requires the knowledge of the resin and fibres density. Then the resin content is measured, and a theoretical composites density is compared to the measured density. This comparison gives, as a result, the void content of the part.

Of course, some interferences of the method are:

- the density resin is assumed to be the same in all the part;
- in composites with high void volume, the error could be around 6-7%, while for those with low content around 0.1-0.2%

The procedure should be carried out in certain conditions:

- the specimen has to be at 23±2ºC and 50±10 % of humidity and the atmosphere laboratory at 23±2ºC with 50±5 % of humidity;
- the volume of the specimen should be higher than 2 cm^3

Once verified these conditions, it is possible to go on with the procedure. The dimension of the specimen has to be carried out with a micrometre with a tolerance on the accuracy about ± 0.0013 cm. So, once calculated the volume and weighted the sample, it is possible to obtain the actual density.

To obtain the void content these steps have been done: with the data on the datasheet of the material , the theoretical density T has been determined: (J. E. Little) (Abdalla F. H., 2008) (W. G. McDonough, 2004)

$$T = \frac{100}{\frac{R}{D} + \frac{r}{d}}$$

Where:

T: theoretical density,

R: % of the weight of resin in composite,

D: density of resin,

r: % of the weight of fibres in composite,

d: density of fibres.

Table 17-Datas to determine the density of samples

	R [%]	D [g/cm^3]	r [%]	d [g/cm^3]	T [g/cm^3]
Panel 14	28.14	1.15	71.85	1.81	1.55
Panel 20	24.98	1.15	75.02	1.81	1.58
Panel 23	24.45	1.15	75.56	1.81	1.58
Panel 24	26.59	1.15	73.40	1.81	1.57
Panel 26	25.39	1.15	74.61	1.81	1.58

Then, it is possible to calculate the void content comparing the theoretical density with the actual density of the sample:

$$V = 100 \cdot \frac{T - M}{T}$$

Where:

V: % of the volume of the void,

T: theoretical density/,

M: measured density.

The void content has been determined on the panels 14, 20, 23, 24 and 26 and for each panel it was obtained on the samples 1 and 3 (figure 52).

The results of the average for each panel are reported in the table below:

Table 18-Measures of the volume of the samples

	L_1 [mm]	L_2 [mm]	L_3 [mm]	Volume [mm^3]	Weight [g]	Density [g/cm^3]
Panel 14	23.18	38.8	2.59	2329.1	3.474	1.49
Panel 20	22.91	37.77	2.43	2102.5	3.192	1.52
Panel 23	22.65	38.13	2.52	2176.8	3.371	1.55
Panel 24	23.05	38.06	2.57	2257.7	3.353	1.49
Panel 26	23.06	39.64	2.47	2252.0	3.495	1.49

The results of the method are reported in the table below:

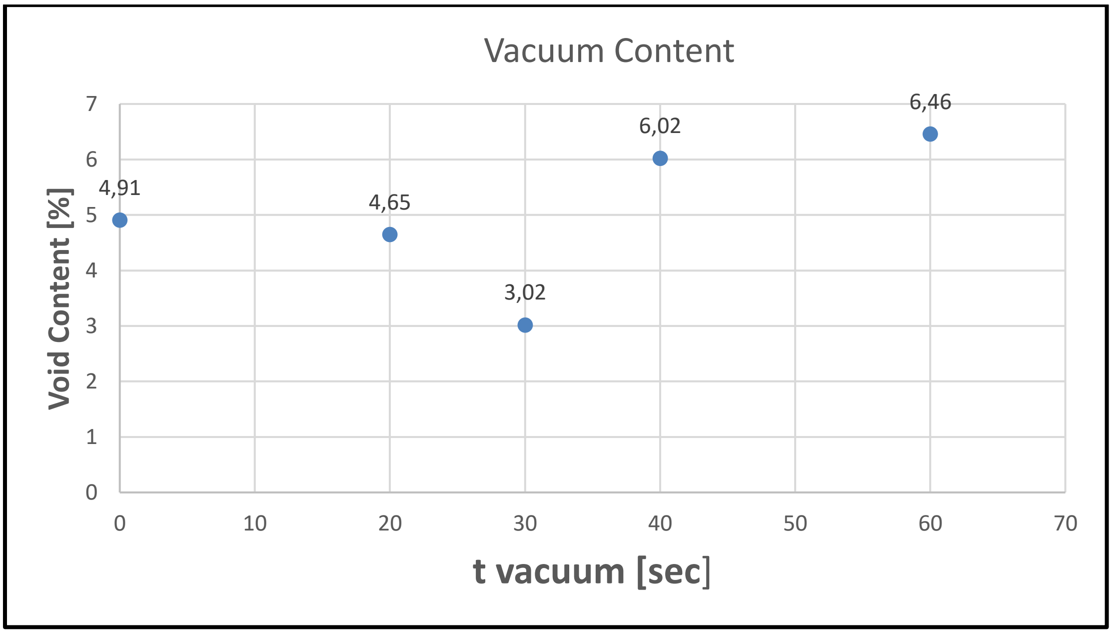
Table 19-Void content

	t_{vacuum} [sec]	T [g/cm^3]	M [g/cm^3]	V [%]
Panel 14	0	1.55	1.49	4.9
Panel 20	20	1.58	1.52	4.6
Panel 23	30	1.58	1.55	3.0
Panel 24	40	1.57	1.48	6.1
Panel 26	60	1.58	1.49	6.5

What emerges by analysis the results of the void content is that the panel with the lowest void content is the number 23 with a timing of application of the vacuum of 30 seconds. Looking to the panel 23 and 26, it is possible to understand the negative effect of the vacuum supply: generate bubbles into the resin.

The chart below reports the content of void according to the timing of application of the vacuum:

Table 20-Void content with different timing of vacuum



4.2 Fiber Volume Fraction Determination

The fiber volume fraction is a really important parameter in the parts since it is the main responsible for the mechanical properties of the manufactured.

The determination of the fiber fraction could be done according to a graphical method and to a chemical method called digestion. (Green, 1991).

Graphical method

The graphical method consists in the determination of the fibers content with the use of a microscope analyzing the cross and polished section of the specimen. (S.C. Yen)

Zooming on the section is possible to see the fibers and the void content, so, with an analytical-graphical method, the fiber fraction is determined. The procedure can be done counting the numbers of fibers in an area of the section and the total area by the average diameter.

The fiber volume fraction is given by the expression:

$$V_f = \frac{A_f}{A}$$

Where:

A_f: area of the fibers

A: area of the portion of the section considered.

The picture below is representative the method:

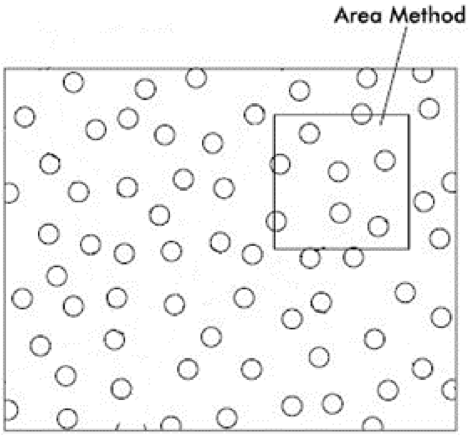


Figure 65-Graphical fiber volume fraction (Mazumdar, 2002)

Using the microscope, some pictures of the cross-section have been analyzed in such way to see the fibers.

The picture below is one exaple of what said before:

Figure 66-Microscope analysis

What it is easy to see, is the presence of few words between the matrix (black regions) and a quite good spread of the fibres between the resin.

On this picture, thanks to the use of an image processing software "IMAGE J" the cross sections have been analyzed to determine the fibre volume fraction.

A total of ten random rectangles have been drawn on the scans, and thanks with the clear colour of the fibers compared to the matrix, the area of the fibers in each rectangle has been calculated.

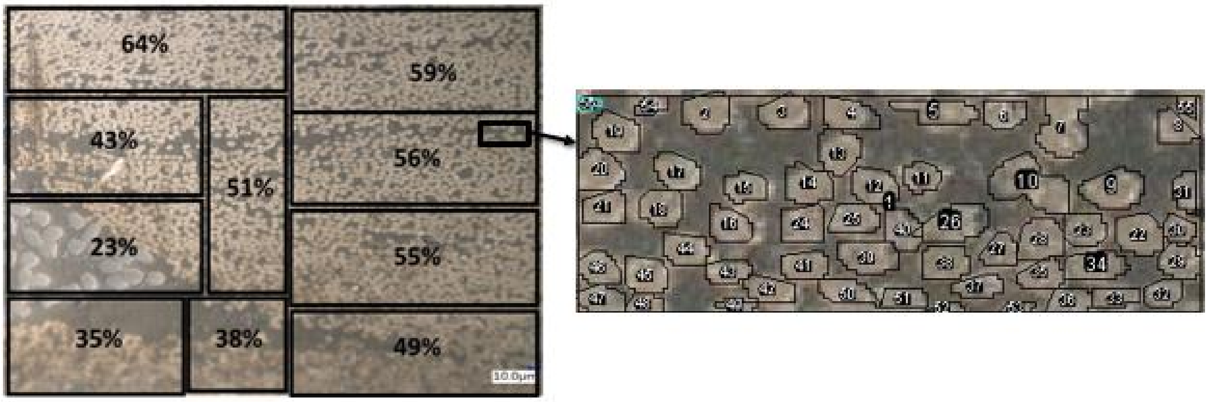


Figure 67-Fiber volume fraction graphical method

Some regions are not exactly rounded by a clear line which means that this method cannot be used as the real value of fiber fraction but just an idea.

The operation of calculation the fiber volume fraction by the graphical method has been applied on different cross sections areas taken by different panels (shown in the appendix B) and comparing all the regions with the fibers area, the final result is a fiber volume fraction ~52% which is an acceptable value considering that the theoretical value should be around 53%.

Digestion method

The digestion method is recognized by the ASTM-D3171 and consists of a determination of fibers content removing the matrix by the effect of acid. (Hassan, 2013)

To proceed with the application of the digestion method, the following tools are required:

- micrometre capable of reading 0.001 mm;
- caliber capable of reading the lenght of the specimen with 0.1% accuracy;
- weight scale capable of reading to the nearest 0.0001 g;
- 70% of nitric acid;
- backers;
- an oven capable of reach 100 ºC;
- filtering apparatus like sintered glass filter;
- distilled water;
- acetone.

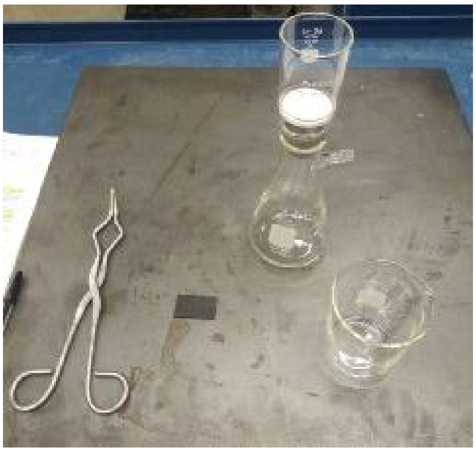


Figure 68-Tools digestion method

The procedure of the method is explained below: first of all, it is necessary to weight the specimen o the nearest 0.0001 g; each specimen is placed in a beaker with the acid and a constant heat source (oven) brings the temperature up to 80 ºC.

Figure 69-Filtered fibers

After the matrix is clearly dissolved in the acid, it is possible to filter the fibers, wash them with distilled water, acetone and then dried into an oven.

Figure 70-Dried fibers after Digestion

After that, when the fibers reach the room temperature, it is possible to weight them.

To determine the fibre fraction, the reinforcement content in weight percent must be calculated:

$$W_r = \frac{M_f}{M_i} \cdot 100$$

Where:

M_i : an initial mass of specimen;

M_f : a final mass of specimen after combustion.

After that, it is possible to calculate the reinforcement content in volume percent:

$$V_r = \frac{M_f}{M_i} \cdot 100 \cdot \frac{\rho_c}{\rho_r}$$

Where:

ρ_c: density of specimen;

ρ_r: density of reinforcement.

With the same procedure the matrix content and the void content are determined:

$$V_m = \frac{M_i - M_f}{M_i} \cdot 100$$

$$V_v = 100 - (V_m + V_r)$$

Where:

V_m: matrix content;

ρ_m: density of the matrix;

V_v: void content.

Two samples have been analyzed to determine the fibre content.

The final results are reported in the table below:

Table 21-Fiber volume fraction

	M_f [g]	M_i [g]	V_r [%]
Sample 1	2.11	3.19	53.3
Sample 2	0.73	0.47	52.9

So, as expected, the fiber fraction content for a panel with 2.5 mm of thickness is about 53%.

4.3 DMA Analysis

The Dynamic Mechanical Analysis or DMA is a technique used to determine the viscoelastic behaviour of the material. The final goal of the DMA is to understand the glass transition temperature for that material by which it is possible to notice some differences with the theoretical one. ASTM D7028. (Foster, 2018)

A deformation is applied to the sample in a cyclic way, so it is possible to evaluate the stress with variations of temperature. What makes DMA different to the TMA is the fact that a sinusoidal force is applied to the sample while in the TMA it is applied a constant static force.

So, as said before, in DMA a cyclical force is applied to the sample of calculated dimensions, and by that it is possible to measure the stiffness, parameter for the elastic behaviour of the material, and the damping, parameter for the viscous behaviour of the material.

The test has been done as a 3-point bending technique: which is a common experiment for the characterization in mechanics. The beam (samples) is supported by two constraints and the load is applied in the middle:

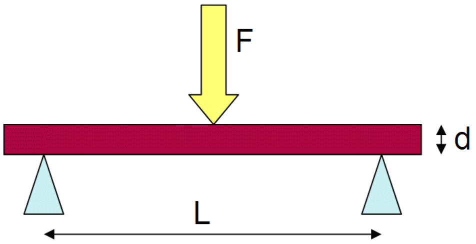


Figure 71-Scheme of 3-point bending test

The temperature is increased from 80ºC to 150ºC with a range of increasing of 5ºC/min and the responses of the material are measured.

The output that comes out from the DMA are:

- in-phase component, the storage modulus (E‘);
- out of phase component, the loss modulus (E’’).

The Storage modulus (E‘) is a measure of the elastic response of the material and so it is a parameter for stored energy. The Loss modulus (E’’) is a measure of the viscous response of a materialso it is a parameter for the energy dissipated as heat.

The equation that relates the 2 parametres to the constutive equation of the materials is:

$$E = \sqrt{E'^2 + E''^2}$$

Where:

E: Young’s modulus

One important parameter related to the storage modulus and the loss modulus is the tan delta defined as:

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

It is a measure of the damping of the material so the dissipation of energy under cyclic load. Higher is tan delta, higher is the potential energy dissipation so the E’’ has a more importance than the elastic behaviour. Decreasing it means that the elastic behaviour is the biggest component in the material.

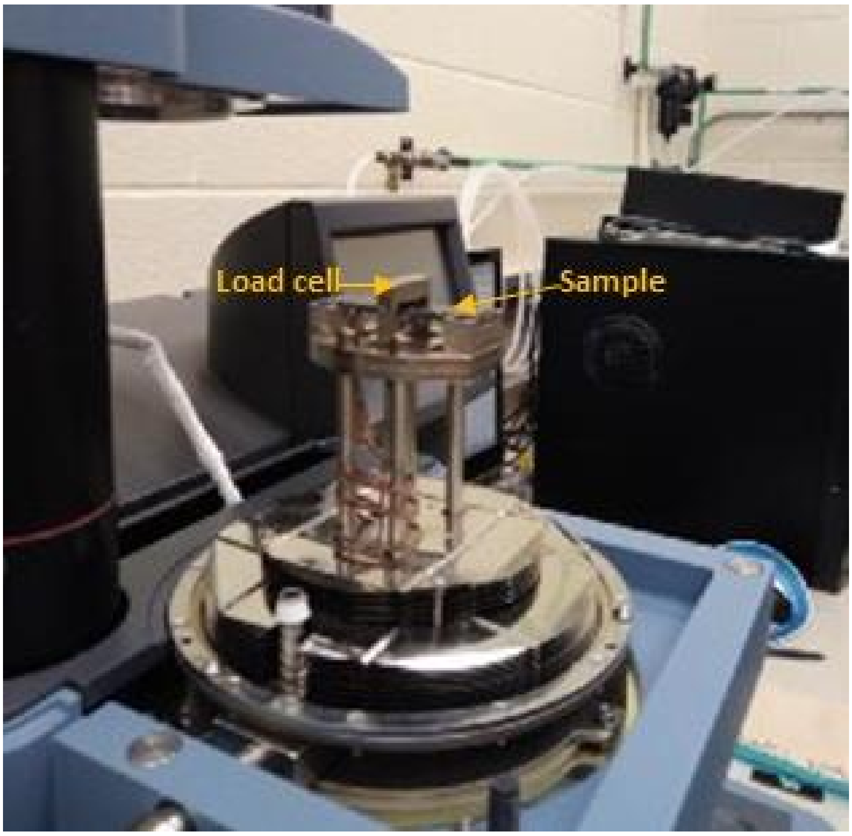


Figure 72-DMA test

The specimen analyzed were taken from the panels 23, 24 and 26 so with a void content respectively of 3, 6 and 6.4%. The dimensions of each specimen were given by the limitations of the machine used for the DMA test, a ‘Q5000 SA’ by the company ‘TA instruments’, and were about 2.5 mm thick, 12 mm wide and 60 mm long.

As said before, the output given by the test are the storage modulus and loss modulus by which it is possible to obtain the damping. The result of these parameters in relation to the temperature for the panel 23 are expressed in the chart below:

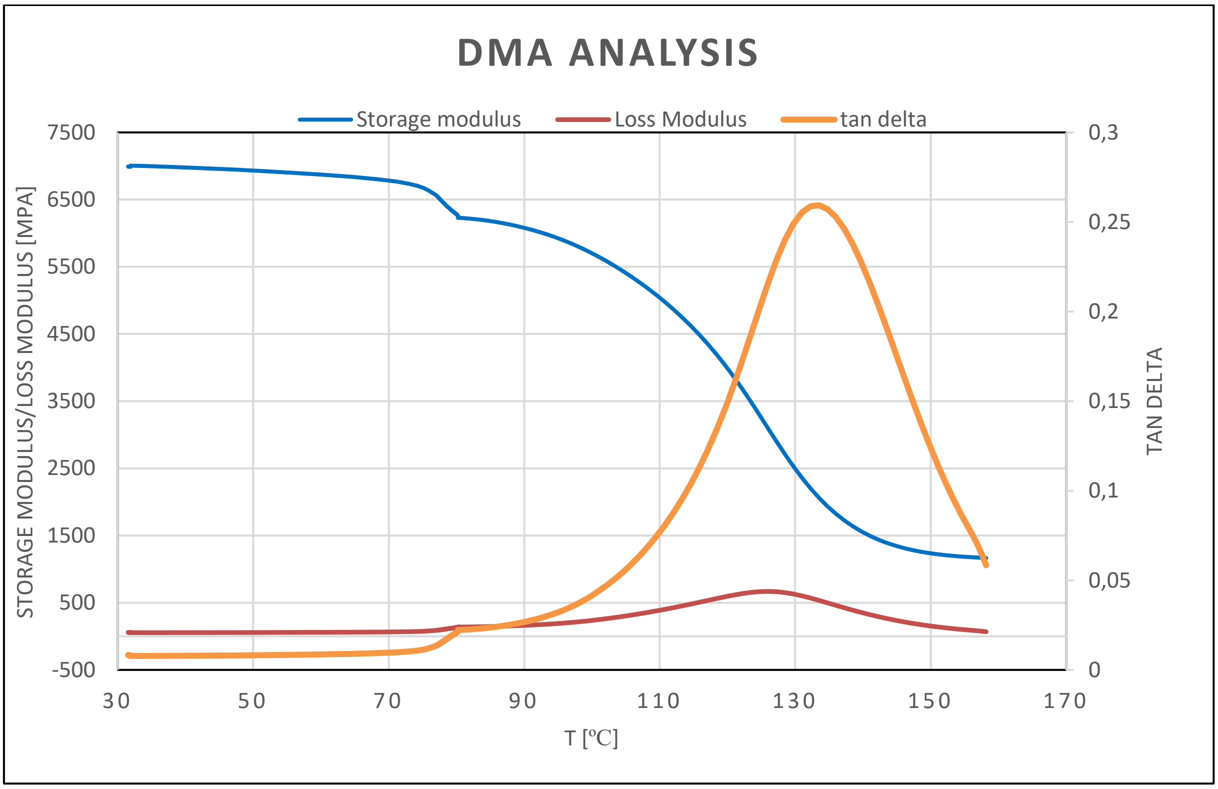


Figure 73-Results of DMA test

The glass transition temperature could be determined according to three different poin of view. It could be defined as the peak of the tan delta, loss modulus or the onset of storage modulus.

That one related to the storage modulus occurs at the lowest temperature and can be interpreted as the mechanical failure. That one related to the loss modulus is between the other two and is connected to the glass transition temperature in the plastic field and shows the molecular processes and the segmental motion of the particles.

Finally, the tan delta temperature, refers to the most common used temperature in the literature and it is connected to behaviour between the rubber and glass state of the plastic (Tainstruments, 2019).

The onset T glass is determined with a graphical method based on the intersection of two tangent lines: the first is selected at temperature before the transition (line 1), the second is constructed at the inflection point to the middle point of the drop of the curve (line 2). Below is shown the determination of the T glass for the panel 23 since the curves are similar between the three panels.

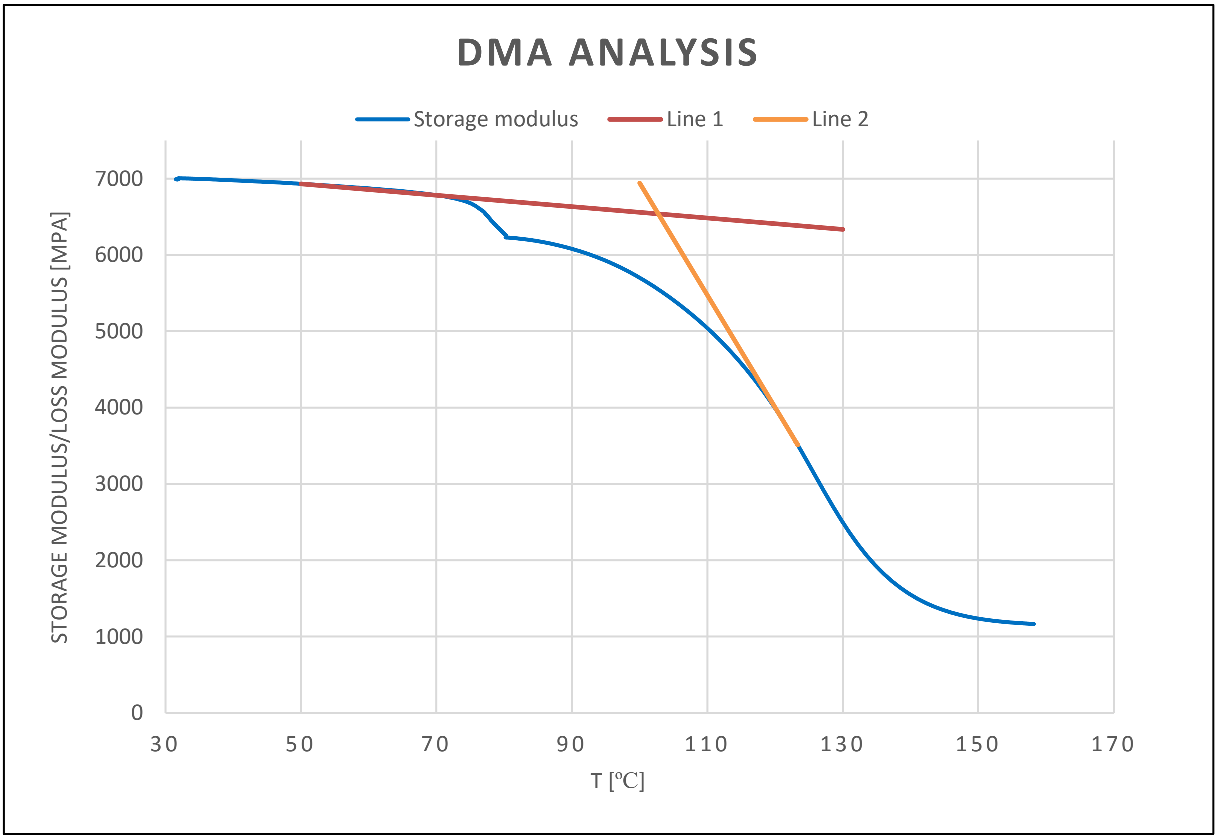


Figure 74-T glass transition with storage modulus

Regarding the other two ways to calculate the glass transition temperature, as said before, they correspond to the peak of the two curves.

The final results of the DMA analysis for the different panels are shown in the table below:

Table 22-Results of DMA test

	T_g-Storage modulus [ºC]	**T_g-Loss modulus [ºC]**	**T_g-Tan delta [ºC]**
Panel 23	102.7	125.9	133.5
Panel 24	102.1	125.5	131.8
Panel 26	104.6	126.6	133.1

The datasheet of the material provided by the company Hexion for the 6150-system shown a glass temperature transition of 118±2ºC for the Onset and 124±2ºC as a midpoint. The test is, obviously, different and it can explain in part the difference in the values but the other factor that has influenced the temperature is the presence of the fibers in the sample that can influence the level of temperature. What emerges from the table is that the void content has no influence on the glass temperature transition that can be defined to be between 100ºC to 133ºC.

Appendix A. Standard Operating Procedure (SOP)

EQIPMENT NAME	Super E Metering Unit
SUPPLIER	Rook Metering Equipment Inc. (Michael Engineering Ltd.)
DESCRIPTION	Automatic Metering unit to mix and dispense 2 different components (e.g., resin + hardener)
LOCATION	E3-2136
PRINCIPAL INVESTIGATOR (PI)	Prof. John Montesano
SOP CREATION DATE	Nov. 26, 2018
SOP CREATED BY	Francesco Mariano
SOP CHECKED BY	John Montesano, Andy Barber

Figure 75-Metering Unit

Only trained and authorized personnel may use this equipment. Reading this SOP is NOT considered training and DOES NOT authorize the reader to use the equipment. This SOP is intended to provide an overview of the metering unit components, recommended safety precautions, steps required to operate the unit (sequentially in Sections 2-4) and cleaning requirements (Section 5).

Significant Hazard	▪ Pressurized air supply may cause injury ▪ Materials mixed by the unit may be toxic ▪ Acetone used to flush unit is volatile and may cause respiratory issues
Administrative Controls	▪ Can only be used during standard working hours. After-hours, two people must be present to operate this machinery.
PPE Required	▪ Protective gloves ▪ Safety glasses ▪ Safety coat (optional) ▪ Protective mask (in case of toxic materials)
Accident Procedures	▪ In case of an accident, please remain calm, attempt the Emergency Shutdown and call for help
Emergency Shutdown Procedure	▪ The Emergency Shutdown Procedure is to engage the E-STOP switch off the control panel located on the front of the machine

Unit Composition

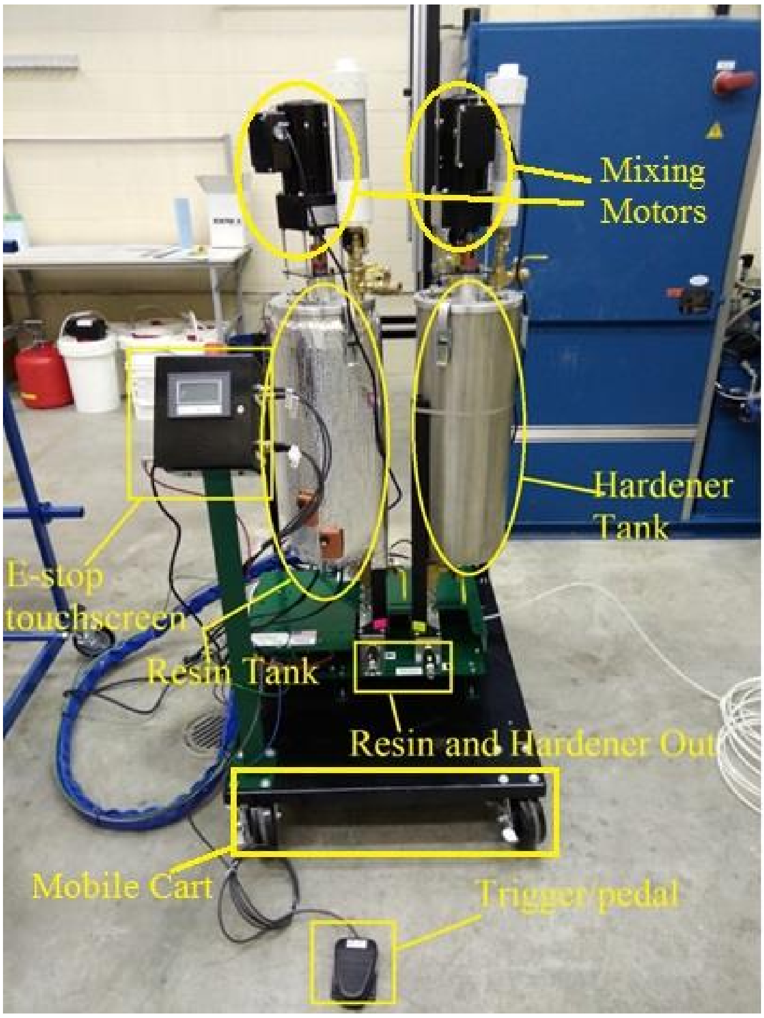


Figure 76-Metering Unit Parts

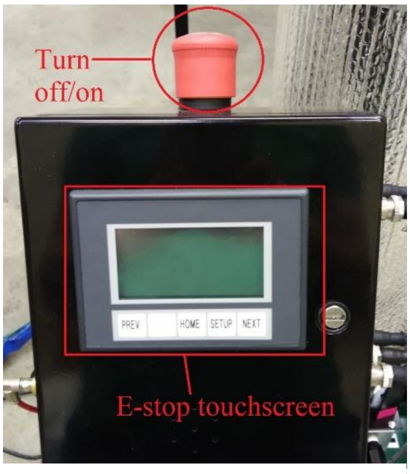


Figure 77 E-Stop Contol

Figure 78-Air-in and Pressure Adjustment

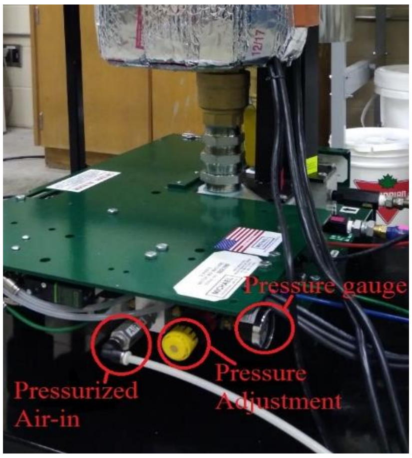


Figure 79-Pressure Adjustment

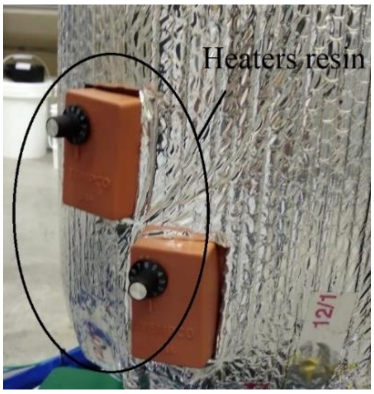


Figure 80- Resin Tank Heat

Figure 81-Tank Valves

Safety Guidelines

It would be impossible to cover every situation that could arise in the use of the machine, this data is not intended to be complete, nor is it presented in any particular order of importance. It is good, safe practice to evaluate the safety concerns of every molding setup and operating procedure **before** starting the machine.

General and specific safety guidelines and cautions are included here and throughout the manual for your protection and to help avoid injury to you and to your co-workers. You are responsible for evaluating the total manufacturing process and identifying and implementing the best method of protecting the operator from injury at the point of operation.

It is your responsibility to immediately report any unsafe condition or unusual machine performance to your supervisor.

A1.1 General Operating Safety

A knowledgeable and well-trained Department technical staff or student is responsible for safety requirements, regulations and enforcement.

The safety coordinator must investigate all accidents and "close calls". The causes should be analyzed, corrective action taken and accurate records maintained.

The procedures to be followed in case of accidents are specified in this SOP, while a list of relevant names, addresses, and phone numbers who are to be notified are also included.

Do not allow a machine to be operated if it is poorly maintained, malfunctioning or in need of guards or safety devices that protect the operator from potential hazards.

Pay strict attention to all caution, warning, and danger signs located on the unit.

Never leave the machine running unattended for any length of time.

A1.2 Safeguarding the Point-Of-Operation

It is the PI's and operator's responsibility to evaluate each setup and to determine and implement the best method of protecting the operator from injury at the point-of-operation.

Each molding application must be examined and evaluated to determine which type of safeguarding and safety device offers maximum operator protection.

Never allow machine guards or safety devices to be bypassed or removed.

Evaluate all point-of-operation guards, safety devices and work procedures frequently while the machine is in operation. Immediately correct any unsafe condition.

A1.3 Supervision and Safety Enforcement

Operators must abide by all safety rules and regulations. To make machine safety effective, every violation should be reported.

Conduct frequent inspections of the machine operations. Be sure the operator and helpers are using proper safety devices and are working safely.

Never allow machine guards or safety devices to be removed, altered or bypassed.

Never allow untrained personnel to operate the machine.

Never allow personnel who are under the influence of drugs or alcohol, or otherwise not physically or mentally alert, to operate the machine.

Be alert to unsafe machine or operating conditions. A poorly maintained machine or a machine that is malfunctioning should be shut down until the safe condition has been corrected.

A1.4 Inspection and Maintenance

To maintain a high level of machine reliability and to obtain advance warning of any possible hazards or malfunctions, a monthly program of machine inspection and preventive maintenance must be followed and documented.

Auxiliary equipment and safeguards must be inspected and maintained in safe operating condition.

Never perform maintenance or repair work until you are sure the unit power is turned off.

A1.5 Training

All personnel who will be associated with the operation of the machine must read and have complete understanding of the contents of this SOP and the unit operation manual.

Personnel must be properly trained prior to using the unit, including standard operations and safety.

A1.6 Safety Guidelines for Operators

- **BEFORE STARTING MACHINE:**

Never operate the machine until you have read and fully understand the safety, control description and operating sections in this manual.

Inspect the machine before each use for loose, worn or broken parts. Report any unsafe conditions to your supervisor immediately and do not operate the machine until the necessary repairs are made.

An important part of machine safety is good preventive maintenance. Keep your machine clean and in good condition by cleaning daily.

Clean your work area frequently. Keep it uncluttered and free of loose tools, discarded work pieces, rags, wires, oil, grease, water or anything that can inhibit your movement or cause you to trip or fall.

Be sure machine guards and safety devices are correctly installed in their proper position.

Never attempt to bypass or remove any point-of-operation guard or safety device on your machine. They are there for your protection.

Be alert for possible hazards or safety irregularities that could cause injury.

STARTING MACHINE:

Before you start the machine, be sure you know how to stop it instantly.

Report any unsafe condition or unusual machine performance to your supervisor.

- ### MACHINE OPERATION:

Pay attention to the warning tags on the machine. They are there for your benefit.

Do not reach around, under or over any guards while the machine is running.

Never bypass, remove or alter any machine guards or safety devices.

Use care and judgment in the work you are doing. Take the time to evaluate the operation **- Is it safe? Are you working a safe procedure?**

Stay alert at all times. Do not become overconfident and careless. Avoid inattention, pre-occupation and distractions.

If you leave the machine for any length of time, always check to make sure the set-up parameters are as you left them before restarting the machine. They may have been modified during your absence.

Know who or where to call for immediate help in the event of any emergency or injury.

Have all injuries treated, no matter how small.

A2. Prechecking Unit Prior to Use

A2.1 Storage Tank Vacuum Test

A vacuum test is required to ensure that both storage tanks are properly sealed (never use a positive pressure). Using a vacuum pump with a hose attached to the appropriate tank connector (see Figure 7), pull the maximum vacuum with no material in the tank. Note that only the vacuum valve on the tank lid should be open during this procedure. The pressure indicated on the tank gauge should reach 27-29 inches of Hg. Once the vacuum test is completed, release the vacuum in the storage tanks.

Figure 82- Vacuum Controller

A2.2 Pressurized Air Supply

Ensure that the pressurized air supply is on and set to the desired pressure, and that the air hose is connected to the metering unit (see Figures 3 and 4). The typical minimum pressure required to operate the unit is 80 psi.

A2.3 Power Supply

Ensure that all metering unit cables are connected to the power bar located on the mobile cart base. The power bar can be connected to a standard 110V power outlet. Note that once power is supplied to the unit, some components (e.g., hoses, manifold/gun) will begin to heat immediately to predefined temperatures; caution must be taken to avoid injury. Ensure that the power bar is switched on only when the unit is ready to operate.

A3.Operation Settings

A3.1 Filling the Storage Tanks

To fill the tanks, at first it is necessary to understand the role of each valve on the storage tank lid.

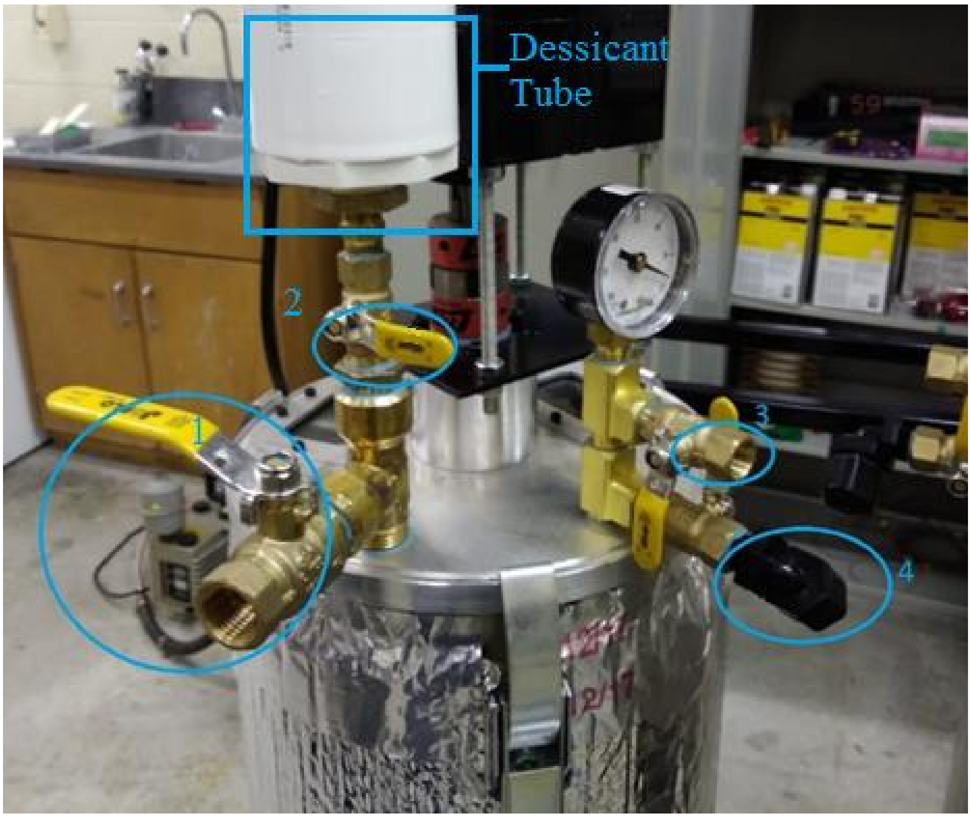


Figure 83-Valves on the lid

The function of the valves numbered 1 to 4 are:

1-Material intake valve used when filling the tank

2-Clean and dry air input valve used to return the tank to atmospheric pressure after degassing the material (<u>MUST BE OPEN WHILE DISPENSING</u>)

3-Nitrogen intake (not used)

4-Valve used to pull vacuum during tank filling or degassing.

The procedure to fill each tank is as follows:

Ensure that resin is filled into the insulated tank and hardener (curing agent) into the non-insulated tank; the subsequent steps are applicable for both tanks

Valve 1 should be opened and have a ¾” diameter hose connected to it. The hose is acting like a large straw that is in the pail of material sitting on the floor (see Figure 11).

Open Valve 4 approximately ¼ of the way and start pulling a vacuum on the tank. It is possible to adjust valve 4 so as to pull a high vacuum on the tank while still sucking the material into the tank.

Only two valves should be open during filling, the material inlet valve (1) and the valve for pulling the vacuum (4).

Do not fill the tanks more than half for the degassing procedure.

Note that after filling the tank, the ¾” diameter hose should be removed from the connector at Valve 1 and the valve should be closed. [Placeholder: The hose may be cleaned after use; however, it is advisable to use a new hose every time the tanks are filled.]

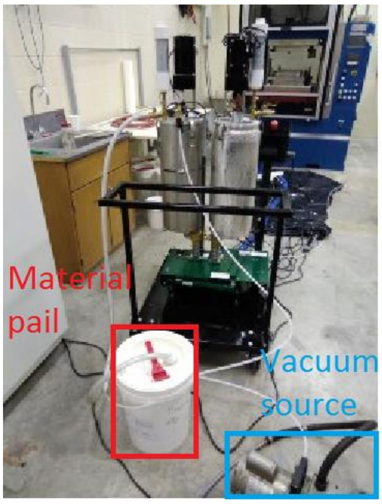


Figure 84-Filling the tank

A3.2 Storage Tank Temperature Control

The insulated resin tank is equipped with 2 band heaters. On the knob of each tank heater control there is a scale from 0 to 10, where 1=90º F; 2=100º F;… 10=180º F. The resin tank temperature should be set prior to degassing to allow the resin viscosity to decrease.

Figure 85-Tank heater controllers

A3.3 Degassing the Material

After filling the tanks and allowing the resin to heat, if necessary, activate the motors to mix the material inside each tank and then turn off them of before proceeding with the degassing procedure. Note that typically the resin tank would require degassing only if air is introduced during tank filling, while the curing agent does not typically require degassing since it has a low viscosity.

Secure the lid using its latches and close the following valves (refer to Fig. 8): makeup air (2), material in (1), and nitrogen intake (3). Only the valve connected to the vacuum source should be open. Note that the seal under the tank lid should be properly positioned before securing the lid.

Turn on the vacuum pump to degas. During degassing the material may rise and foam, thus care should be taken so that the material is not drawn into the pump. It is possible to observe the degassing progress using the window on the top of the storage tank lid as showed in Figure 12. The pump pressure can be adjusted to limit foaming of the material and to control the degree of degassing.

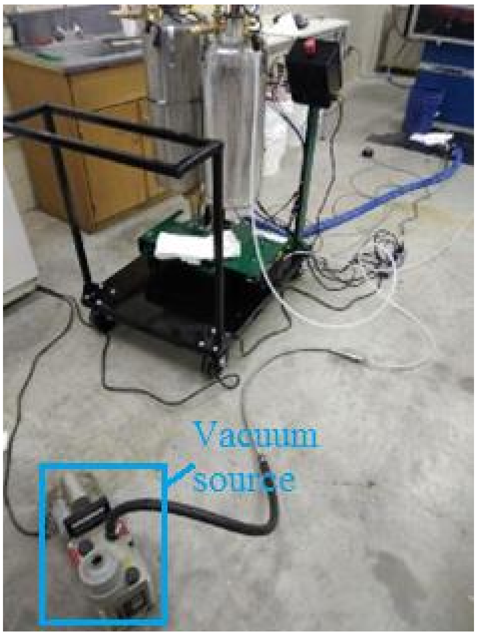


Figure 86-Degassing

Figure 87-Rising and foam of the resin

After degassing, the vacuum must be released prior to dispensing material.

A3.4 Check and Change the Mixing Ratio

Prior to checking the mixing ratio, disconnect the hoses from the storage tank output connectors (see Figure 1). **Ensure that the air pressure valve (Fig. 3) is open and the desired pressure is set, and that valve 2 (Fig. 8) on the storage tank lids are open with all other valves closed prior to dispensing material**. Place 2 cups, 1 under the resin tank output and 1 under the hardener tank output, and dispense one shot. Then, weigh each cup and check the ratio. Since the metering unit dispenses material with a mixing ratio based on volume, ensure that the weight of each material component is converted to volume. See Appendix A for a sample calculation. Note, purging may be required prior to checking the mixing ratio.

It is necessary to slide the non-insulated tank and pump to adjust the mixing ratio. There are 4 bolts that must be loosened: 2 underneath and 2 behind the pump of the non-insulated tank.

The operator can refer to page 18 of the unit User Manual for mixing ratio adjustment data.

Figure 88-Bolts under the non-insulated tank pump

Figure 89-Bolts behind the non-insulated tank pump

A3.5 Purging the Hoses

Stretch the hoses out (no hills or valleys). Dispense material without the gun until both the resin and hardener are free of air. (It will take 10-20 full strokes).

Figure 89- Stretched hoses connected to the Unit

A3.6 Check Timing

Correct machine timing is achieved when both materials begin dispensing at the same time. If timing is not correct “off ratio” material will be dispensed.

The Air Cylinder Side pump is adjustable for timing adjustment. Located at the end of the air cylinder side pump is a Timing Block Adjustment Bolt. This Bolt is turned Clockwise to retard the air cylinder side material and turned counter clockwise to advance the air cylinder side material.

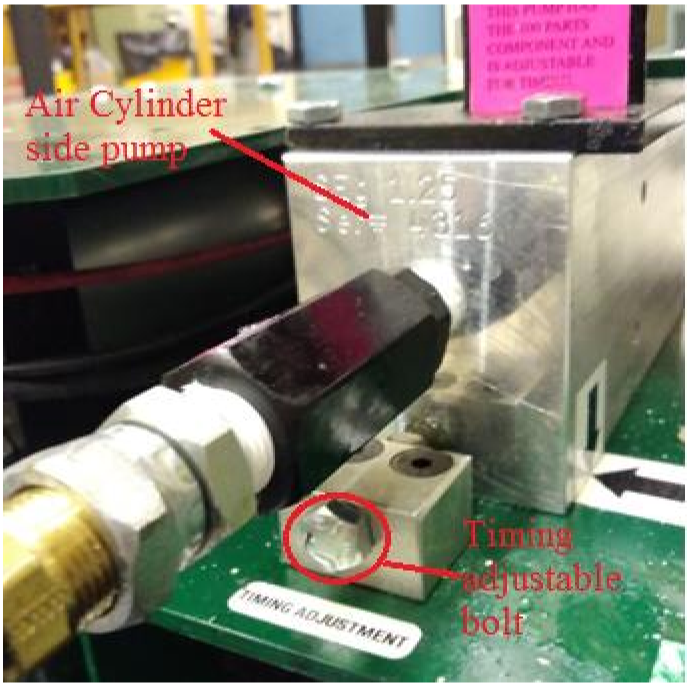


Figure 90-Air cylinder side pump and pivot side material

Figure 91-Adjustable bolt

If the air cylinder side pump starts first, its timing must be retarded; if the pivot side material starts first then the air cylinder side pump must be advanced.

-To retard the air cylinder side pump: loosen the 2 pump mounting bolts, located on the back of the machine (equivalent of those in Fig.13 for the air cylinder side pump), one turn. Turn the timing bolt clockwise. Check timing and make adjustment as needed. Tighten mounting bolts.

-To advance the air cylinder side pump: follow the same procedure above, only turn the timing bolt counter-clockwise.

To check the timing, pump a small amount of the 2 components out of the hoses with the gun disconnected; both materials have to begin dispensing at the same time.

A4. Operating the Super E

Once the air has been purged from the Super E, the timing and ratio had been verified, it is possible to dispense the material. Note that the resin tank should be heated as required prior to dispensing.

Select the appropriate static mixer and install it on the manifold/gun (place some grease on the manifold threads).

Figure 92-Manifold with static mixer

Open the air pressure valve (Fig.3), set a pressure of 80 psi (minimum value of pressure to use the gun) (Fig.4), turn on the E-stop and open valve 2 (Fig.10).

To dispense the material, it is possible to choose a running continuous mode or single shot mode (normal trigger or latched trigger - read below).

When the E-stop is turned on, the first menu is “Home” where it is possible to set the shot size. Press “Setup” to access on the menu to set Purge mode, Auto repeat, Set timing, Normal trigger, Stats and so on. See the instructions in the User manual for specific use (page 56 to 64).

Once every required parameter has been set, push the pedal to dispense the material.

A4.1 Check Shot Size

As a final operation prior to performing a trial, it is important to verify the shot size.

Once the shot size has been set on the E-stop touchscreen and the gun has be connected to the hoses, place 1 cup under the gun and dispense 1 full shot. By knowing the density of the components in the tank and the set mixing ratio, it is possible to check the shot size weighting the cup with the 2 mixed components (see appendix A as example).

A5. Cleaning and Maintenance

The following operations should be performed to clean the metering unit after daily use during multiple day trials (Section 5.1), or when it is required to remove material from the storage tanks after long-term use or at the end of a trial (Section 5.2).

A5.1 Daily Cleaning

After a day of processing trials when material will remain in the storage tanks, only the manifold/gun must be cleaned. First, remove the static mixer and dispose of it. Pump a small amount of material out of the manifold, wipe off any material and soak for a full cleaning (unscrew the manifold from the gun - see schemes below).

Put a small amount of grease in the cap and put the cap on the manifold to seal out the air.

Clean the pintles by advancing the snuff-back adjustment until the pintles are visible from the seat plate.

A5.2 Cleaning After Removing or Switching Material

When removing material from the metering unit storage tanks after the completion of a trial or after long-term use, the remaining material should be dispensed from both tanks and the unit should be flushed with acetone as per the following procedures.

Dispensing material: The E-stop controller can be used to dispense all material from the tanks. If the material will be reused, the hoses can be removed and each material dispensed into clean separate containers. Otherwise, the mixed material can be dispensed into a container and properly disposed.

Flushing with acetone: To flush with acetone, pour enough solvent in the tanks to cover the intake port. Run the machine until solvent is dispensing from the manifold/gun. Remove the gun and point the hoses back into the corresponding tanks to recycle material. Run the unit until the resin is well dissolved and then drain the tanks and pumps. Put fresh solvent and run again with the hoses in the reservoirs. Once the tanks and connections are clean, drain acetone out of the machine and dispose appropriately.

For all of these operations, it is mandatory to wear protective masks for organic vapour, gloves and safety glasses. Keep attention on the electrical plugs: the acetone is flammable and volatile.

Note, if the metering unit will be stored and not used for 3 weeks or more after flushing with acetone, the "Long Term Unit Storage" section below should be consulted to prevent corrosion. If the metering unit will be stored for less than 3 weeks, no action is required after flushing and removing all traces of acetone.

Also note, during long-term use of the metering unit material can only remain in the tanks for a maximum of 3 weeks otherwise the isocyanine may crystalize in the pump and lines and the unit will have to be disassembled to remove crystalized material. See "Long Term Use" section below for details.

a. Long Term Unit Storage

If the unit will be stored and not be used for 3 weeks or more after flushing with acetone, you will need to remove any residual of the solvent immediately after flushing. Introduce a small amount of Mesamoll oil in the tanks and dispense until all acetone is expelled from the pumps and lines and clear Mesamoll comes out of the manifold/gun. Note that during storage the tanks should contain a small amount of Mesamoll oil, while the lines, pumps and hoses should be filled.

Prior to using the machine after long-term storage, pump out the Mesamoll oil and proceed with filling the storage tanks with material.

b. Long Term Use

For continual usage of the unit during multiple day trials, material can remain in the tanks for a maximum of 3 weeks after which the unit must be flushed with acetone. Ensure that material is dispensed at least once per week during this time; this will prevent the curing agent from blocking the pump/piston below the uninsulated tank. To avoid wasting material at the end of the three-week period, the tanks should be initially filled with enough material required for the trials to the best of the operator's ability. As a note, avoid storing the curing agent in the presence of oxygen to limit the speed of degradation; ensure the corresponding tank is always sealed.

Appendix B. Microscope Analysis

In the appendix below are shown, as expressed before, all the picture that have been used to determine the fiber volume fraction with the graphical method (paragraph 4.2).

Figure 93-Cross section 1

Figure 94-Cross section 2

Figure 95-Cross section 3

Figure 96-Cross section 4

Figure 97-Cross section 5

Figure 98-Cross section 6

Figure 99-Cross section 7

Figure 100-Cross section 8

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