ATLÂNTICA - Escola Universitária de Ciências Empresariais, Saúde,

Tecnologias e Engenharia

DEVELOPMENT, MANUFACTURING AND TRANSFORMATION OF THERMOPLASTIC COMPOSITE MATERIALS BASED ON CONTINOUS CARBON FIBER AND LOW-DENSITY THERMOPLASTIC MATRICES

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Dissertação orientada pelo Professor Doutor D. Bartolomé Miguel Simonet Suau

MASTER´S DEGREE IN MATERIALS ENGINEERING

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May 2019
ATLANTICA, Escola Universitária de Ciências Empresariais, Saúde, Tecnologias e Engenharia

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1. SUMMARY

A composite is a material that is formed by combining two or more distinct materials, of which one is a binding material (known as matrix) and the other is a reinforcement material (which is generally a fiber). The matrix can be metallic, ceramic, or polymeric. The fiber can be carbon, glass, aramid, or natural. Resins are required to hold the fiber and bind material together while the fiber provides structure and strength to the composite. Composites that are manufactured using thermoplastic matrix are considered as thermoplastic composites.

Thermoplastic composite is one of the fastest-growing composite materials used in various applications, such as transportation, aerospace & defence, Electricals & electronics (E&E) and consumer goods, among other applications. In terms of value, the thermoplastic composite market size is mainly dominated by short fiber reinforcement thermoplastic (SFRT) and long fiber reinforcement thermoplastic (LFRT).

Environmental regulations for low CO2 emissions and fuel efficiency mandates in Europe and the U.S. dictate more fuel-efficient vehicles from 2015. Thermoplastic composites are seen as substitutes for aluminium and steel in high-end cars that would help the automotive industry to meet the fuel efficiency standards. The demand for lightweight thermoplastic composites is being driven by an increasing emphasis on fuel efficiency in the whole transportation market. In addition, in other specific industries like the aerospace & defense, they are further pushing the inclusion of lightweight material in aircrafts. For them, short cycle manufacturing times and materials with high impact resistance are key to increase the penetration of thermoplastic composites in the aeronautical sector. Other additional important advantage of thermoplastic is that they are recyclable materials.

However, the adoption of thermoplastic composites is lagging, due mainly to their high costs and manufacturing complexity. The high cost of thermoplastic composites is a major concern associated with their growth. There are a large number of applications of thermoplastic composites that are not commercially viable due to their high cost. The development of low-cost technologies is a major challenge for all manufacturers of thermoplastic composites specially for structural components.

At present, the most extended manufacturing process for plastic composites is based on thermosetting. A thermosetting plastic, also called a thermoset, is a plastic that is irreversibly cured from a soft solid or viscous liquid prepolymer or resin. The process of curing changes the resin into an infusible, insoluble polymer network, and is induced by the action of heat or suitable radiation often under high pressure, or by mixing with a catalyst. The production process based on thermosetting allows high flexible designs, high levels of dimensional stability and cost-effective production costs. However, this process has 3 main limitations: 1) can only be heated a once and; 2) cannot be remolded or reshaped: If re-heated they cannot soften as polymer chain are interlinked. They are made of a fixed molecular structure that cannot be reshaped by heat or solvents that are joined by adhesives. 3) Cannot be recycled.

Market’s state of the art for the production of thermoplastics are based on the use of plastic, generally in the form of powder, and application of pressure and temperature in the melting conditions of the thermoplastic mat to achieve the fusion of the same and the integration with the fiber in the presence of vacuum and atmosphere inert.

Comparatively, thermoplastics provides different advantages: 1) can be heated and shaped many times; 2) it can be remoulded, 3) It is recyclable and eco-fiendly manufacturing. However, this procedure has 2 main constraints: it requires time and energy, which translates into a high-cost raw material (stack).

This work has been focused in thermoplastic composites based on continuous carbon fibers and low-density thermoplastic matrices. Concretely, it will be studied the combination of carbon fibers with the thermoplastic matrices such as polypropylene, polyethylene and polyamide. With this material, it will be studied the process to manufacture and transform them into a composite having adequate fiber to plastic ratio, good homogeneity and the absence of air bubbles. For that the effect of the main industrial parameters of the proposed process will be studied and optimized. The composites obtained will be tested in order to characterise their main mechanical properties. Finally, these experimental properties will be compared with the theoretical ones obtained from properties of the fiber and the plastic matrix. It is, the properties calculated by applying the theory of self-consistent field. This approach will allow to present son general comments regards interaction of the fibers with the plastic matrix, the modification of plastic properties dues the process as well as advantages and limitations of the studied manufacturing process.

RESUMO

Um compósito é um material que é formado pela combinação de dois ou mais materiais distintos, dos quais um é um material de ligação (conhecido como matriz) e o outro é um material de reforço (que é geralmente uma fibra). A matriz pode ser metálica, cerâmica ou polimérica. A fibra pode ser carbono, vidro, aramida ou natural. As resinas são necessárias para manter a fibra e unir o material, enquanto a fibra fornece estrutura e resistência ao compósito. Os compósitos fabricados com matriz termoplástica são considerados compósitos termoplásticos.

O compósito termoplástico é um dos materiais compostos que mais cresce em diversas aplicações, como transporte, aeroespacial e defesa, Eletroeletrônicos (E & E) e bens de consumo, entre outras aplicações. Em termos de valor, o tamanho do mercado de compósitos termoplásticos é predominantemente dominado por termoplástico de reforço de fibra curta (SFRT) e termoplástico de reforço de fibra longa (LFRT).

Regulamentações ambientais para baixas emissões de CO2 e mandatos de eficiência de combustível na Europa e nos EUA ditam veículos mais econômicos em combustível a partir de 2015. Compósitos termoplásticos são vistos como substitutos do alumínio e do aço em carros de alto desempenho que ajudariam a indústria automotiva a atender a eficiência de combustível. padrões. A demanda por compósitos termoplásticos leves está sendo impulsionada por uma ênfase crescente na eficiência do combustível em todo o mercado de transporte. Além disso, em outros setores específicos, como o aeroespacial e de defesa, eles estão empurrando ainda mais a inclusão de material leve em aeronaves. Para eles, tempos de fabricação de ciclo curto e materiais com alta resistência a impactos são fundamentais para aumentar a penetração de compósitos termoplásticos no setor aeronáutico. Outra vantagem adicional importante do termoplástico é que eles são materiais recicláveis.

No entanto, a adoção de compósitos termoplásticos está atrasada, devido principalmente a seus altos custos e complexidade de fabricação. O alto custo dos compósitos termoplásticos é uma das principais preocupações associadas ao seu crescimento. Há um grande número de aplicações de compósitos termoplásticos que não são comercialmente viáveis devido ao seu alto custo. O desenvolvimento de tecnologias de baixo custo é um grande desafio para todos os fabricantes de compósitos termoplásticos, especialmente para componentes estruturais.

Atualmente, o processo de fabricação mais extenso para compósitos plásticos é baseado em termofixas. Um plástico termoendurecível, também chamado de termoendurecível, é um plástico que é irreversivelmente curado a partir de um pré-polímero líquido ou resina macia, sólida ou viscosa. O processo de cura altera a resina para uma rede polimérica insolúvel e infusível e é induzida pela ação do calor ou radiação adequada, freqüentemente sob alta pressão, ou pela mistura com um catalisador. O processo de produção baseado em termoendurecimento permite projetos altamente flexíveis, altos níveis de estabilidade dimensional e custos de produção econômicos. No entanto, este processo tem 3 principais limitações: 1) só pode ser aquecido uma vez e; 2) não podem ser reformados ou remodelados: se forem reaquecidos, eles não podem amolecer, pois a cadeia polimérica está interligada. Eles são feitos de uma estrutura molecular fixa que não pode ser remodelada pelo calor ou solventes que são unidos por adesivos. 3) Não pode ser reciclado.

O estado da arte do mercado para a produção de termoplásticos baseia-se no uso de plástico, geralmente na forma de pó, e na aplicação de pressão e temperatura nas condições de fusão do tapete termoplástico para conseguir a fusão do mesmo e a integração com a fibra na presença de vácuo e atmosfera inerte.

Comparativamente, os termoplásticos oferecem vantagens diferentes: 1) podem ser aquecidos e moldados muitas vezes; 2) pode ser remodelado, 3) É reciclável e ecologicamente correto. No entanto, este procedimento tem duas restrições principais: requer tempo e energia, o que se traduz em uma matéria-prima (pilha/stack) de alto custo.

Este trabalho foi focado em compósitos termoplásticos baseados em fibras de carbono contínuas e matrizes termoplásticas de baixa densidade. Concretamente, será estudada a combinação de fibras de carbono com matrizes termoplásticas como polipropileno, polietileno e poliamida. Com este material, será estudado o processo de fabricação e transformação em um compósito com relação fibra / plástico adequada, boa homogeneidade e ausência de bolhas de ar. Para isso, o efeito dos principais parâmetros industriais do processo proposto será estudado e otimizado. Os compósitos obtidos serão testados para caracterizar suas principais propriedades mecânicas. Finalmente, essas propriedades experimentais serão comparadas com as teóricas obtidas a partir das propriedades da fibra e da matriz plástica. Ou seja, as propriedades calculadas aplicando a teoria do campo autoconsistente. Essa abordagem permitirá apresentar a todos os comentários gerais sobre a interação das fibras com a matriz plástica, a modificação das propriedades plásticas do processo e as vantagens e limitações do processo de fabricação estudado.

2. OBJECTIVE

Composites are materials increasingly used due to their characteristics and properties. Despite its great interest, they use have been limited mainly to the development of thermostable matrices. In recent years, due to the environmental interest, the development of composites based on thermoplastic matrices are acquiring special interest. For that, the aim of this work is focused on composite thermoplastic materials making special attention to their development including a study of their physical and chemical properties, a description of potential manufacturing process to obtain in a simple way these materials and finally a description, study and optimization of the transformation process to manufacture parts from these materials.

This general objective will be finalized in the combination options between carbon fiber fabrics and low-density thermoplastic polymer matrices such as:

- Polyamide 6
- Polypropylene
- Polyethylene

3. STATE OF ART

Thermoplastics can be combined with short, long, or continuous fibers of different natures including carbon or glass fibers to obtain composites.

The "pyramid of excellence"[1] arbitrarily classifies the main families of thermoplastics according to their performances, consumption level and degree of specificity:

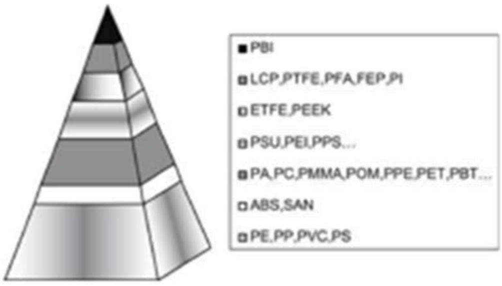

Figure1. Pyramid of excellence for some thermoplastic families

3.1 Thermoplastic vs. thermoset composites

Polymers are classified as thermoplastics or cross-linked polymers such as elastomers or thermosets. Thermoplastics polymer can be either amorphous (without regular structure), or semicrystalline (amorphous base structure with embedded regular substructures).[2]

Thermoplastics have the simplest molecular structure, with chemical independent macromolecules. By heating, they are softened or melted, then shaped, formed, welded,

[1] Michel Biron. (2013). *Thermoplastics and Thermoplastic Composites*.

[2] E. Murat Sozer. (2003). Process Modelling in Composites Manufacturing.

and solidified when cooled. Multiple cycles of heating and cooling can be repeated without severe damage, allowing reprocessing and recycling.

Often, some additives or fillers are added to the thermoplastic to improve specific properties such as thermal or chemical stability, ultra violet resistance, etc.

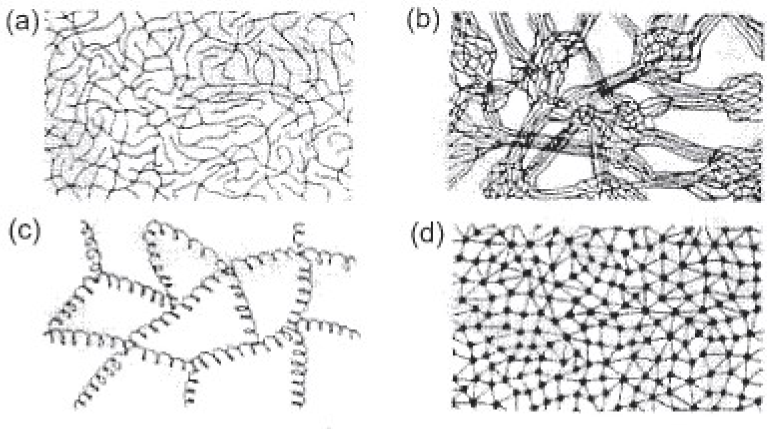

Figure 2. Schematic of the molecular structure: a) Amorphous Thermoplastic, b) Semi-crystalline Thermoplastic, c) Elastomer and d) thermoset[2]

Mainly, the first and most obvious difference between a thermoplastic and a thermoset polymer is the need for heat application to melt the first. The manufacturer, as a rule, provides the thermoplastic matrices in solid state; so, it is necessary to apply heat to melt it and therefore, start a phase change from solid to liquid, either before the start of the manufacturing process or during the manufacturing process. After processing, the thermoplastic melts and must be cooled to solidify it, while the thermoset become a solid after it is chemically and thermally activated to form a reticulated network, which is also known as curing. In addition, it is usually necessary to add a diluent to the thermosets to lower their viscosity.

Thermoplastics at room temperature are solid, but their viscosity around the processing is between 10^2 and 10^6 Pa.s. Also, thermoplastics exhibits non-Newtonian behaviour such as shear thinning of the viscosity with applied stress, whereas thermosets are relatively insensitive to shear. All polymers exhibit reduction in viscosity with temperature, although thermoplastics can exhibit a steeper reduction than thermosets.

The thermoset materials once cured cannot be re-melted or reformed. During the curing stage, they form three-dimensional molecular chains, called cross-links. Due to these cross-links, the molecules are not flexible and cannot be reshaped or remodelled. The greater the number of cross links, the more rigid, the more thermally stable the material will be. In rubbers and other elastomers, the densities of cross-links are much lower and therefore flexible.

Thermosets are fragile in the environment and are generally used with some type of filler and reinforcement. The thermosetting resins provide easy processability and better impregnation of the fiber because the liquid resin is used at room temperature for several processes such as filament winding, pultrusion and RTM. The thermostable offer greater thermal and dimensional stability, better rigidity and greater electricity, chemistry, and resistance to solvents.

The most commonly used thermosetting resins are epoxy, polyester, vinyl ester, phenolics, cyanate esters, bismaleimides and polyimides. Some of the basic properties are shown in the following table[3]:

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[3] Sanjay K Mazumdar. (2002). *Composites manufacturing materials, product, and process engineering. CRC Press.*

Table 1.Typical Unfilled Thermosetting Resin Properties

Resin Material	Density (g/cm^3)	Tensile Modulus GPa (10^6 psi)	Tensile Strength MPa (10^3 psi)
Epoxy	1.2–1.4	2.5–5.0 (0.36–0.72)	50–110 (7.2–16)
Phenolic	1.2–1.4	2.7–4.1 (0.4–0.6)	35–60 (5–9)
Polyester	1.1–1.4	1.6–4.1 (0.23–0.6)	35–95 (5.0–13.8)

In contrast, thermoplastic materials are, in general, ductile and stronger than thermosetting materials and are used for a wide variety of non-structural applications without fillers and reinforcements. Thermoplastics can be melted by heating and solidified by cooling, which makes them capable of repeated remodelling and reforming. The thermoplastic molecules do not crosslink and therefore are flexible and reformable.

As mentioned, thermoplastics can be amorphous or semicrystalline. In amorphous thermoplastics, the molecules are randomly arranged; whereas, in the crystalline region, the molecules are arranged in an orderly manner. It is not possible to obtain 100% crystallinity in plastics due to the complex nature of the molecules.

Below are some properties of thermoplastic resins:

Table 2.Typical unfilled thermoplastic resin properties[4]

Resin Material	Density (g/cm³)	Tensile Modulus GPa (10⁶ psi)	Tensile Strength MPa (10³ psi)
Nylon	1.1	1.3–3.5 (0.2–0.5)	55–90 (8–13)
PEEK	1.3–1.35	3.5–4.4 (0.5–0.6)	100 (14.5)
PPS	1.3–1.4	3.4 (0.49)	80 (11.6)
Polyester	1.3–1.4	2.1–2.8 (0.3–0.4)	55–60 (8–8.7)
Polycarbonate	1.2	2.1–3.5 (0.3–0.5)	55–70 (8–10)
Acetal	1.4	3.5 (0.5)	70 (10)
Polyethylene	0.9–1.0	0.7–1.4 (0.1–0.2)	20–35 (2.9–5)
Teflon	2.1–2.3	—	10–35 (1.5–5.0)

Thermoplastic composites do not enjoy the highest quality and a high level of integration as is currently obtained with thermosetting systems. In market terms, thermoset matrices dominate the market over thermoplastics. About 75% of all composite products are made of thermosetting resins. In addition, manufacturing processes with thermosetting composites are much more mature than their thermoplastic counterparts due mainly to the widespread use of thermoset composites, as well as their advantages over thermoplastic composite processing techniques.

In the table below, you can see a summary of the differences between thermoplastics and thermosets from processing viewpoint[5]:

[4] Sanjay K Mazumdar. (2002). *Composites manufacturing materials, product, and process engineering. CRC Press.*

[5] E. Murat Sozer. (2003). *Process Modelling in Composites Manufacturing.*

CHARACTERISTICS	THERMOPLASTICS	THERMOSETS
Viscosity	High	Low
Initial State	Usually solid	Usually liquid
Post processing	None	Heat neccesary
Reversibility	Can be remelted and re-formed	Once formed, virgin state cannot be recovered
Heat transfer requirement	Heat needed to melt it	Heat may be need to initiate cure
Processing temperature	Usually high	Can be at room temperature
Usage	Large volumes in injection molding	Mainly used in advanced composites
Solidification	Cooling for change of phase	Chemical reaction

Table 3.Summary of differences between thermoplastics and thermosets from processing viewpoint

3.2 Properties and characteristics of thermoplastics and thermoplastic composites

Polymers have some specific properties due to their organic nature. Thermoplastics are independent organic macromolecules with some sensitivity to environmental parameters: temperature, moisture, deleterious solids, liquids, gasses, and other chemical products. They are also sensitive to mechanical loading, especially cyclic loads. Their specific properties, such as electrical as optical properties, are also important for their applications.

All the properties are influenced by the additives used with thermoplastic matrices, notably the reinforcements but also stabilizers, plasticizers, colorants, and other.

Thermomechanical behavior is most probably the most widely exploited property of engineering thermoplastics. The figure shows the behavior of two types of thermoplastic, one amorphous and the other semicrystalline, versus temperature. We can see several steps moving from low to high temperatures[6]:

- A high modulus plateau corresponding to a brittle material
- A first decrease of the modulus that depends on the material morphology:
    - Leading to a ductile state for amorphous material
    - Leading to a second pseudo-plateau for the semicrystalline thermoplastic
- A final drop for the semicrystalline material

This is important for the majority of applications because:

- The softening at “high” temperature limits the mechanical performances
- The brittleness at low temperature can lead to failure after light impacts
- The damping properties broadly vary with temperature and become weaker or non-existent at low temperatures.

The selection of thermoplastics and composites to design a new part requires impartial and comparative testing methods.

[6] Michel Biron. (2013). *Thermoplastics and Thermoplastic Composites.*

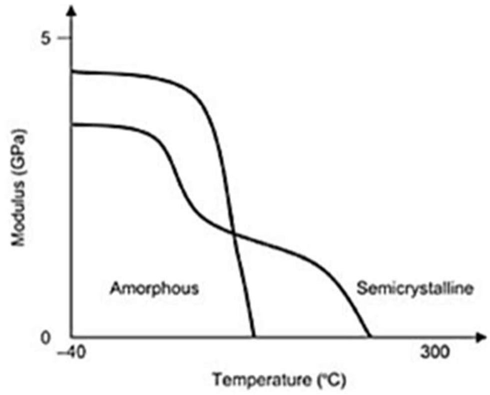


Figure 3.Examples of modulus variations versus temperature for an amorphous and semicrystalline thermoplastic[7]

3.2.1 Thermal behaviour

A temperature rise causes two different phenomena:

- Immediate physical effects:
  - Decay of the modulus and other mechanical and physical properties, physicochemical softening
  - Dimensional stability: reversible thermal expansion and, eventually, irreversible shrinkage and warpage
- Long-term effects
  - Physical: irreversible creep and relaxation to a greater or lesser extent
  - Chemical: irreversible degradation of the material, decrease in mechanical properties, even after a return to the ambient temperature.

[7] Sanjay K Mazumdar. (2002). *Composites manufacturing materials, product, and process engineering. CRC Press.*

The maximum service temperatures depend on the duration of service time and the possible simultaneous application of mechanical stresses.

A fall in temperature has only physical effects:

- Increase in the modulus and rigidity
- Reduction in the impact resistance; the material can become brittle
- Eventually, crystallization for semicrystalline polymers

3.2.2 Density

Density is a basic characteristic of thermoplastics, important for engineering, economic, and structural reasons:

- Weight saving is one of the reasons leading to polymer choice
- Density is a consequence of structure and allows low-, medium-, and high-density polyethylene material to be distinguished
- Prices are based on weight, and often, the part design is based on volume.

For dense thermoplastics, densities are in the range of o,8 g/cm³ to more than 2,0 g/cm³. For cellular materials such as foams, densities can be as low 10 kg/m³.

3.2.3 Mechanical properties

A lot of characteristics are currently deduced from the stress/strain curves. The figure shows the case for two tensile behaviors:

- One for a brittle polymer, when the break point arises immediately after the yield point or coincides with it
- The other for a ductile polymer, when the break point is far from the yield point

Although resulting from low speed tests, these curves give results only under instantaneous loads whereas in real life the parts are exposed to log-term stresses or strains. For this, it is necessary to refer to the long-term mechanical properties.

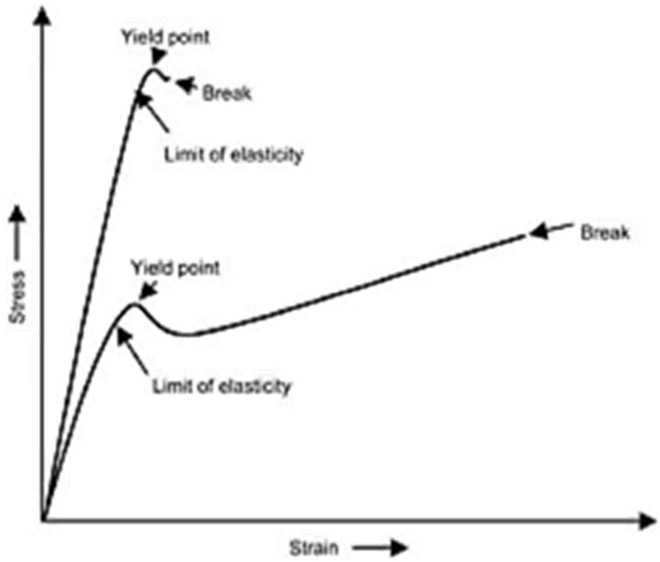


Figure 4.Tensile behavior polymers

Conventional mechanical measurements are:

- Elastic modulus: is the slope of the tangent at the origin of the stress/strain curve. The tensile or compression modulus is often called Young´s modulus, whereas the torsion modulus is often called shear modulus or Coulomb`s modulus.
- Yield point: Is the first point of the stress/strain curve for which there is an increase in the strain without an increase in the stress. Parts must always operate well below this point during service.
- Stress and strain at yield: are the values of the stress and strain corresponding to the yield point.

- Ultimate stress and strain: are the value of the shear strength producing a delamination between two composite layers along the plane of their interfaces
- Impact test: measure the energy absorber during a specified impact of a standard weight striking, at a given speed, a test sample clamped with a suitable system. The results depend on the molecular orientation and the degree of crystallization of the material in the sample, its size, the clamping system, the possible notch and its form, the mass, and the strike speed.

The loading types generally used now are:

- Tensile
- Flexural
- Compression. In this case, it is generally a unidirectional compression. Bulk compression is rarely used, except for modelling.

3.3 Main manufacturing processes of thermoplastic composites

As previously mentioned, the initial raw material in thermoplastic composite materials is in the solid state, so it must be melted in order to process it. This implies a series of advantages and disadvantages:

Advantages:

1. There is no chemical reaction during the process, which implies a short process cycle time. This means that they can be used for high production volumes.
   A clear example can be seen in the automotive industry: they have a high production rate and their manufacturing method is injection molding with cycle times of less than 1 minute.
2. Thermoplastic composites can be easily remodelled. Simply the application of heat and pressure is enough to be able to reform them.
3. Thermoplastic composites are easy to recycle.

Disadvantages:

1. Use of heavy and strong tools for the processing of thermoplastic composites. This implies a high cost in tools.
2. Sometimes they require sophisticated equipment to apply heat and pressure, which increases the cost of processing.

3.3.1 Thermoplastic Pultrusion Process

Pultrusion is a continuous, automatic and closed mold process, specially designed for high production volumes, in which case it is economically very profitable. Basically, it consists of pulling the reinforcements impregnated with a thermoplastic matrix, through a mold at high temperature, in such a way that the thermoplastic polymerizes in its interior and profiles of constant section are obtained with the geometry of the mold. The reinforcements are impregnated by means of a bath placed at the entrance of the mold or by injection into the mold.

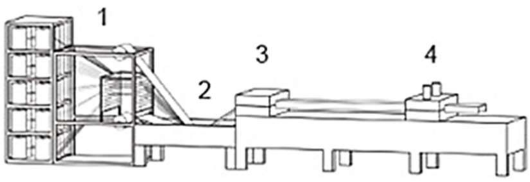


Figure 5. Process scheme. 1) pre-forming the reinforcement fibers; 2) Bucket for impregnation of fibers; 3) Heating mold; 4) Mechanism of traction of the polymerized profile

The pultrusion process is used to obtain solid or hollow pieces of constant section.

Currently the main applications of this process are focused on construction, consumer goods and transport, for example:

- vehicle construction / thermal insulation
- rail technology (train interiors, tracks)
- wireway
- covers and grilles for water treatment plants
- medical technology, antennas (airport masts), satellites
- profiles for beams, facades of buildings, windows, bridges, stairs.
- golf clubs, fishing rods
- lampposts, benches and external boards
- hammer handles, etc.

Figure 6. Pultrusion Profiles

In each market for the application of pultruded materials, these must always compete with traditional materials such as wood, aluminium, PVC (polyvinyl chloride), concrete and steel.

The main advantages of the profiles obtained by pultrusion compared to traditional materials are the following:

- Constant quality and dimensional stability: easy to repair, low tolerances.

- Low weight: these materials are up to 80% lighter than steel and 30% lighter than aluminium, which is why they are an important alternative when reducing weight is a requirement.

- Great strength and rigidity: for a same weight a pultruded composite is more resistant and rigid than steel, simply by varying the type and orientation of the reinforcements.

- Good surface finish

- High chemical and corrosion resistance

- Thermal and electrical insulation

- Due to its excellent properties (corrosion) these materials require no or very little maintenance

- Easy design and installation: due to its lightness

- Magnetic and radiofrequency transparency: suitable for medium applications, antennas, etc.

However, pultrusion also has some drawbacks, the most important ones are listed below:

- High difficulty to manufacture pieces that are not one-dimensional and of constant section.

- The need for a high-performance mold with a very fine finish (so as not to impede the progress of the piece in the process), a heating system and, occasionally, internal pressurization. All this means that the cost of the mold is very high and that very long series of production are needed to amortize it.

- The speed of the process is relatively low compared to the speed of the extrusion.

- Adhesion problems when it is necessary to join pieces with adhesives, due to the fine finishing of the pieces. To obtain high performance joints, it is necessary to prepare the joining surfaces by means of a mechanical pre-process (sanding the surface), chemical (bath with substances that catalyze the adhesion reaction) or adding a peel-ply at the entrance of the mold.

3.3.2 Compression molding

Compression molding is a forming process in which a plastic material and fiber reinforcement is placed directly in a metal mold, heated and then softened by heat, and forced to conform to the shape of the mold in the mold closed.

The process starts by heating the material to a malleable and molded state. Soon after, the hydraulic press compresses the flexible plastic against the mold, impregnating the fiber, resulting in a perfectly molded piece that maintains the shape of the interior surface of the mold. After the hydraulic press backs down, an ejector pin at the bottom of the mold quickly ejects the final piece out of the mold and then the process concludes.

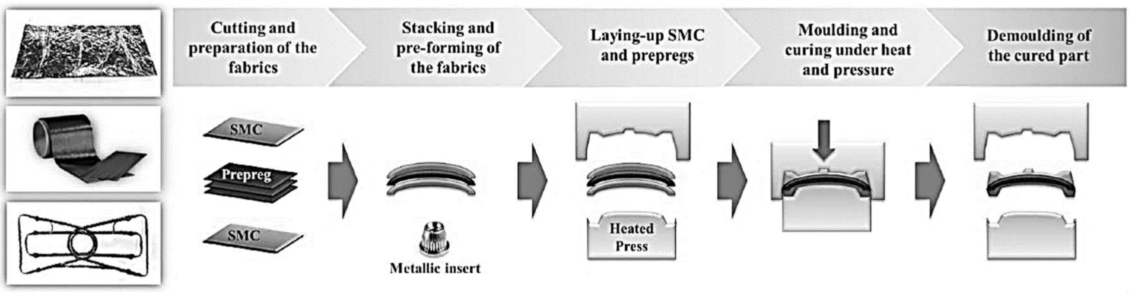


Figure 7. Compression molding process Scheme

PRESSES:

The compression molding presses are oriented vertically and contain two plates to which the mold halves are fastened. The process involves two types of action: 1) ascending stroke of the bottom plate or 2) descending stroke of the upper plate, but the latter is the most common configuration. A hydraulic cylinder generally operates the plates, which can be designed to provide clamping forces of up to several hundred tons. The resin or thermoplastic is added with the preform. The heat and pressure are applied, with temperature ranges necessary to cure or polymerize the pieces. The cycles can vary from less than one minute to five minutes. The machinery consists of a mold "piston" male and a female mold and guide pins that ensure the perfect fit between them. Main applications:

- Automotive and transport: bumpers, crosspieces, inserts for dashboards, phonic shields, seat frames, …
- Storage, handling: containers, tanks
- Miscellaneous: welding helmets, ventilators shells, lawnmower bases

Below are some advantages of the process:

- Fluid in small distances: lower internal tensions.
- Low cost of maintenance and mold manufacturing.
- Simple design of molds, as there is no entrance and channels.
- Allows molding of complex parts
- Good surface finish (in general)
- Relatively low material waste

Disadvantages of compression molding:

- The mold must be kept at not too high temperature, so that the walls do not heal much faster than the inside. Therefore, long curing times.
- Limited shapes: It is not advisable for this method in case of use of molds of complex shapes
- Heavy investments

3.3.3 Processing Long Fiber Reinforced Thermoplastics

The method depends on the fiber length:

- Grades reinforced with fibers 10mm long can be processed on conventional injection equipment by simply adapting processes to preserve the fibers
- Grades reinforced with fibers 20mm or more in length cannot be processed on conventional injection equipment. It is necessary to use, for example, the compression molding or extrusion/compression technique.

Extrusion/compression technique is based in the combination of two basic processes:

1. The thermoplastic composite is heated and plasticized in a screw extrusion machine that feeds a mold.
2. The part is compression molded into the cooled mold

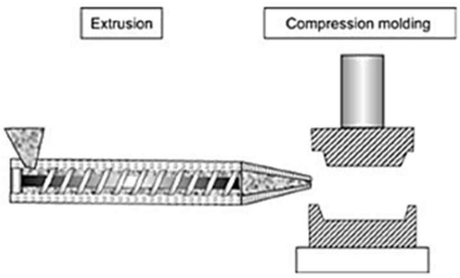


Figure 8.Principle of the extrusion-compression process

Advantages:

- It is possible to user longer fibers than with the injection process

Disadvantages:

- Discontinuous fibers
- Slower than injection molding
- Limited choice of reinforcements
- Higher labor costs
- Specialized equipment

3.3.4 Prepreg Draping and consolidation by vacuum or pressure bag molding, autoclave…

Pre-impregnated rovings, tapes, tows or fabrics, cut to the right shape and size, are laid up by hand or machine onto a mold surface.

- Hand lay up: it is possible to use honeycombs or foams
- Automated lay up: there are numerous degrees of automation with more or less complex machines
- The consolidation is obtained by heat and pressure: vacuum or pressure bag molding, autoclave, …
- Solidification requires cooling

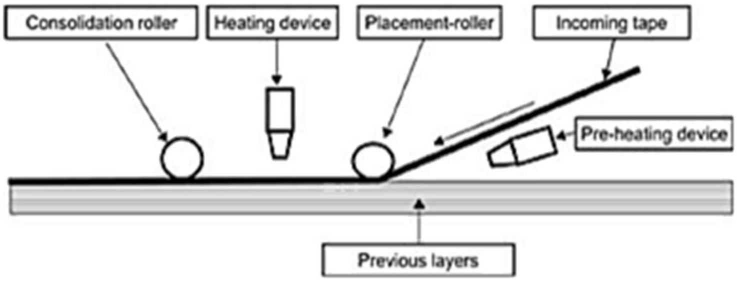


Figure 9. Principle of an automated tape placement machine[8]

Advantages:

- Hand lay up:
  - Design freedom
  - Molding of complex parts with variations of thickness
  - Lower investments
- Automated lay up:
  - Faster than hand lay up
  - Lower labor costs
  - Better repeatability

Disadvantages of the draping process:

- Hand lay up:
  - High labor costs
  - Skilled labor required
  - Risks of placement errors
  - Slow

[8] Michel Biron. (2013). *Thermoplastics and Thermoplastic Composites.*

- Automated lay up:
    - Heavy investments
    - Skilled labor required
    - Limited design possibilities

3.3.5 Filament and tape winding

There are several steps[9]:

1. The impregnated roving or prepreg is heated by a heating head
2. The machine winds up the roving or prepreg on a mandrel, which turns on an axis
3. A post-consolidation can be obtained by heat and pressure: specific pressure device, vacuum or pressure bag molding, autoclave, …
4. Solidification requires cooling

The fibers can be placed:

- Perpendicular to the axis: circumferential winding or 90° filament winding
- Parallel to the axis: 0° filament winding
- Sloped at a defined angle on the axis: helical winding

The mandrel can be recoverable, or can be integrated in the finished part, for example, in the inner liner of high-pressure tanks.

[9] Michel Biron. (2013). *Thermoplastics and Thermoplastic Composites.*

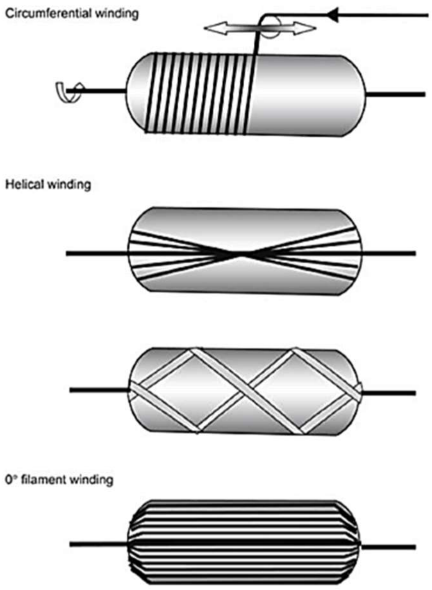


Figure 10.Principle of filament or tape winding

Advantages:

- The reinforcement levels can reach 60% to 75%, even 80%, making it possible to obtain excellent mechanical characteristics
- The properties can be enhanced in chosen directions by modifying the winding angle
- Part sizes can be significant

Disadvantages:

- Heavy investments
- Limited design and shapes
- The reinforcement placement must be carefully calculated

Examples of applications:

- High pressure tanks with metal inner liner
- Piper, masts.

4. MATERIALS AND EQUIPMENT

This section describes the characteristics of the materials used with the description of their characteristics and properties including both the fibers used and the thermoplastic matrices. A description of the equipment used is also presented.

4.1 MATERIALS

4.1.1 CARBON FIBER

Carbon fiber is a synthetic fiber consisting of fine filaments of 5-10 μm in diameter and composed mainly of carbon. Each carbon fiber is the union of thousands of carbon filaments. It is a synthetic fiber because it is made from polyacrylonitrile. It has mechanical properties similar to steel and is as light as wood or plastic. Due to its hardness, it has greater resistance to impact than steel.

The main application is the manufacture of composite materials, in most cases with thermoset polymers although there is a growing percentage of applications with thermoplastic

In all cases, a carbon with generic sizyng compatible with epoxy resin, polyester and vinyl ester has been selected. A standard carbon has been selected in order to use low cost raw material looking for the modification of the matrix for a good interaction matrix.

The carbon fiber fabrics used was:

- Twill fabric 2x2
  Carbon 3K, with a superficial density of 252 gr/sqm

4.1.2 THERMOPLASTICS

As a matrix, different types of plastics used. Next, a brief description of which have been selected:

- Polyethylene (PE)

Polyethylene or PE is one of the most common thermoplastics. Its density is in the range 0.91-0.94 g/cm^3. It is used primarily for the manufacture of packaging. It is commonly used for bags, sheets, films, geomembranes, containers, bottles, etc. The average melting point for commercial low-density polyethylene is typically 115 to 135°C.

Polyethylene is classified into several categories based mainly on its density and branching. Their mechanical properties depend to a great extent on variables such as the extension and type of branching, the crystalline structure and the molecular weight.

In our experimental part, the PE used is powder form, with a size of particles about 0.4 mm maximum; and a film form, with a thickness about 64 µm.

- Polypropylene (PP)

Polypropylene (PP) is a low-cost, low-density, versatile plastic and is available in many grades and as a co-polymer (ethylene/propylene). It has the lowest density (0.9 g/cm^3) of all thermoplastics and offers good strength, stiffness, chemical resistance, and fatigue resistance. Its melting point is normally about 165°C, PP is used for machine parts, car components (fans, fascia panels, etc.), and other household items, and has been pultruded with various reinforcements.

In the experimental part, the PP used is powder form, with a size of particles about 0,4 mm maximum; and a film form, with a thickness around 25 µm.

- Polyamide 6

It is a partially crystalline material that due to its manufacturing process shows great tenacity and resistance, important characteristics if used under load or impact or moderate temperatures. Its density is around 1.14 g/cm³ and its melting temperature is around 220°C

It has a high resistance to shock and fatigue, good resistance to wear and also to low temperatures. The resistance to breakage and bending is very appreciable. Its elasticity allows the absorption of vibrations or impacts, so in the bearings and gears work silently. It has a high softening point and an optimal behavior against atmospheric agents.

In our experimental part, the PA6 used is powder form, with a size of particles about 0,4 mm maximum; and a film form, with a thickness around 25 µm.is:

4.1.3 ADDITIVES

The additives shown below were used in order to improve the viscosity of the thermoplastic matrix and thus favour the interaction with the fiber.

The additives used were:

- SCONA TSEB 2113 GB: Modifier for improved impact strength in polyamide and polyamide glass fiber compounds. Dispersing aid for polyethylene filler compounds. It remains stable in processing temperatures up to 300 °C. About recommended level of use, 5-10 % additive (as supplied) based upon total formulation.
- SCONA TSPE 2102 GAHD: Coupling agent for polyethylene fiber compounds and compatibilizer for PA/PE blends. About recommended level of use, 1-4 % additive (as supplied) based upon total formulation, depending on the fiber content.
- SCONA TPPP 9212 GA: Carboxylated Polypropylene (Maleic Anhydrid). Very effective coupling agent in long and short glass fibre reinforced PP composites. About recommended level of use, ow concentrations of approx. 0,2 – 1,5 wt-%, depending on recipe.

- ICORENE 3545: Is a linear low-density polyethylene specifically developed for rotational moulding. Is a suitable for use in general purpose applications. It has a good balance of properties such as toughness, easy flow and stiffness. Melting temperature: 126ºC. About recommended level of use, 1-4 % additive (as supplied) based upon total formulation, depending on the fiber content.
- ICORENE 4014: Is a polypropylene copolymer that has been specifically developed for rotational moulding. This grade is UV stabilised and suitable for applications requiring high stiffness and high temperature resistance. About recommended level of use, 1-4 % additive (as supplied) based upon total formulation, depending on the fiber content.

4.2 EQUIPMENTS

For the initial tests, a laboratory scale mechanical press was used, of its own design. It has a working surface of 300 x 300 mm and heated plates with 8 resistances, 4 in the upper plate and 4 in the lower plate able to reach a temperature of 300ºC. The temperature control is carried out by external temperature sensors. The closing pressure of the press is around 1.5 bar

Figure 11. Tool for pressing of own design

For the experimental development optimized, a conventional vertical press was used. It is a press with compression capacity of 60 Tn (192 bar). The press has a central hydraulic cylinder with sufficient capacity to apply a maximum closing force on the lashing table above 60 Tn.

The system has a lower plate with threaded holes for the mooring of the mold facilitated by the customer and a superior that moves powered at its point centrally by the hydraulic cylinder and those are guided by 4 chromed columns in each one of its vertices. The plate dimension is 2000 x 1400mm.

The press has a heating/cooling system incorporated.

·General dimension of Mould 900x900x590mm. Cavity dimensions 600x600x2mm.

·The system is provided with a mechanical ejection system.

-Heating System Features.

·36 electric Resistance. Temp Max 300ºC.

·Control PLC Siemens 1.200 with Touch Screen.

·Termocouple Tipo K for Temperature Control.

·Program able to develop heating ramps and Cycles.

-Cooling System Features.

The cooling system is provided by a piping circuit of 10mm of diameter distributed in the mould, in order to decrease the mould temperature as faster as possible.

The liquid used as refrigerant is a mix of 50% Propilenglycol with mixed organic-inorganic antioxidant additives.

·Chiller Supply the piping circuit:

- Cooling capacities from 3 to 32 kW.

- Air cooled condenser.

- Tank, pump (5 bar Pressure) and evaporator made of steel stainless.

- Designed for installation in small spaces.

- Suitable for open and closed circuits.

- Suitable for water temperatures of -5 at + 20 ° C.

- Phase control.

IR System

Adjustable structure for IR Resistance distance to the material. 60 units of IR resistance (500W) able to increase the temperature from 25ºC to 500ºC in 12 min. The IR resistances distribution is divided and controlled in 4 parts. Different temperatures parts could be programmed.

The system is provided with a special frame and springs in order to support the material, and introduce them in the system.

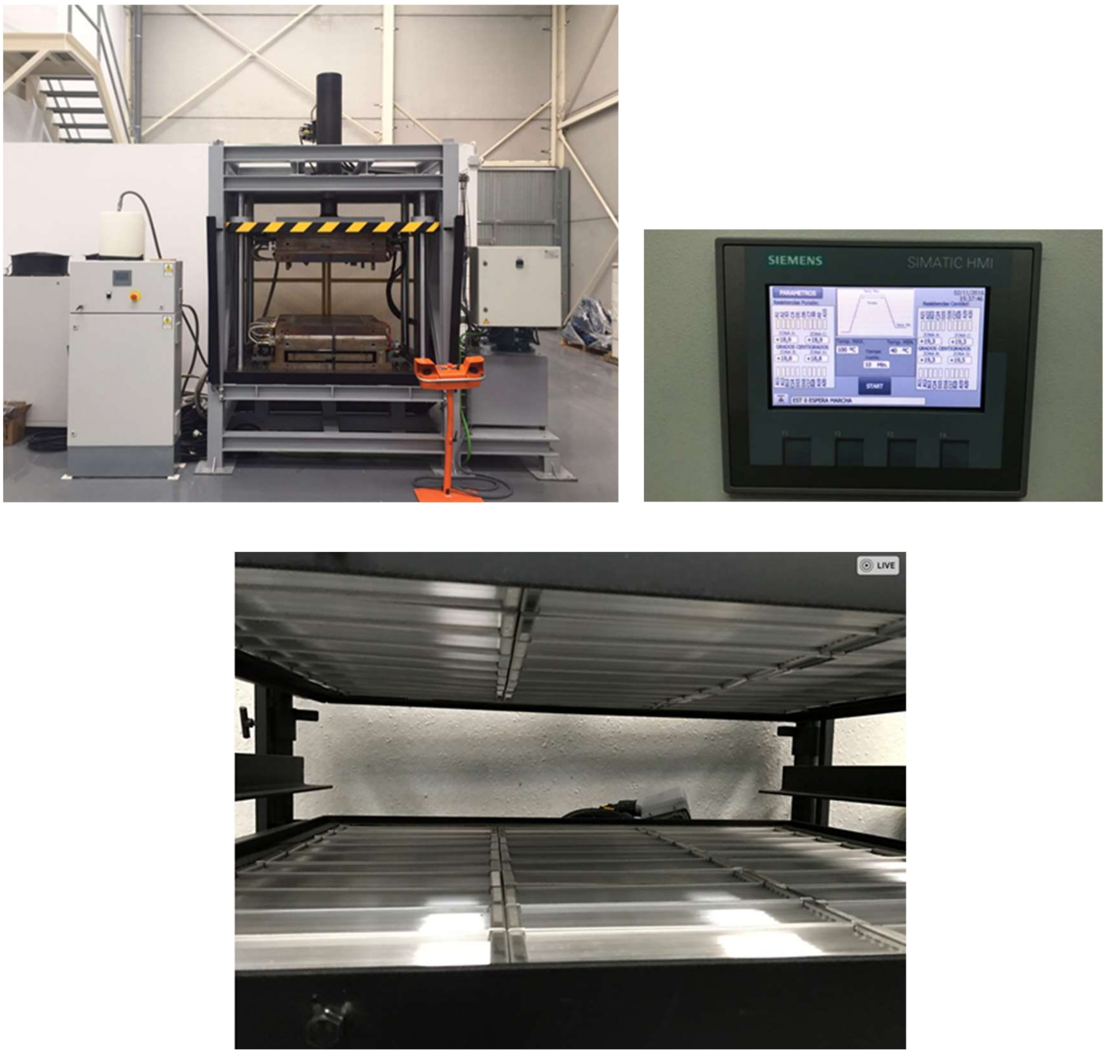


Figure 12. Vertical press of 60 Tons; process monitoring screen

4.3 EQUIPMENT FOR CHARACTERIZATION OF MATERIALS

Material characterization tests have been carried out in external entities and the following equipment has been used:

The first traction tests of the panels manufactured with the mechanical press have been carried out with a Tinius Olsen 10KS Universal Testing Machine. It is used to determine tensile and flexural properties taking as reference the UNE - EN ISO 527 - 1: 1996

(Plastics. Determination of tensile properties. Part 1: general principles), UNE - EN ISO 527 - 4: 1997 (Plastics. Determination of tensile properties. Part 4: test conditions for isotropic and orthotropic fibre-reinforced plastic composites), UNE - EN ISO 1421: 1998 (Rubber- or plastics-coated fabrics. Determination of tensile strength and elongation at break) and UNE - EN ISO 178: 2003 (Plastics - Determination of flexural properties) standards.

It has a load cell of 10,000 N, a maximum distance of 1100 mm between tools, a sample range of 200 Hz (nominal) force and a resolution of the extension reading of 0.001 mm.

For the tests of tensile of the samples manufactured with the vertical press of 60 Tn, a higher capacity equipment was used, with a cell of load about 250 KN.

It has also been used a scanning electron microscope high resolution (SEM) Carl Zeiss Merlin model, with analytical capacity EDX and WDX Oxford is an ultra-high-resolution system that allows to work with all types of samples both in image and in analysis. It consists of a gun of emission of electrons by emission of field of hot tip. It allows a maximum resolution of the secondary electron (SE) image from 0.8 nm to 15 kv, from 1.4 nm to 1 kv and 2.4 nm to 0.2 kv.

5. EXPERIMENTAL SECTION

The experimental works have been structured in four parts:

- Study of the process with mechanical press. Discussion
- Optimized process in vertical press 60 Tn. Process parameters for thermoplastic stack manufacture. Mechanical properties
- Processes of transformation: thermoforming
- Procedure for cutting thermoplastic composites. Water jet

In the first part of the studies we have analysed the manufacturing process of thermoplastic composites, evaluating the manufacture from film and powder in order to conclude which manufacturing process is more efficient to get a good composite in terms of homogeneity, absence of bubbles, fiber compaction and degree of interaction of fiber - thermoplastic matrix. For the latter, plastic matrices modified with chemical agents have also been studied.

This first part was carried out on a laboratory scale with the equipment described above (mechanical press).

From the results of this analysis it has been concluded that the process should be approached from the industrial point of view. Specifically, it has been selected:

- Polyethylene
    - PE powder + additive TSPE 2102 + fiber twill
    - PE powder + ICORENE 3545 additive + fiber twill
- Polypropylene
    - PP powder + fiber twill
    - PP film + fiber twill
    - PP powder + TPPP 9212 additive + fiber twill
    - PP powder + ICORENE 4014 additive + twill fiber

- Polyamide
    - PA powder + fiber twill
    - PA film + fiber twill
    - PA powder + additive TSEB 2113 + fiber twill

Evaluated thermoconsolidation processes to obtain stack of thermoplastic composite of continuous fibers, the study of the fabrication of elements by thermoforming is addressed. This study is addressed in section 5.3 in which three geometric shapes have been defined.

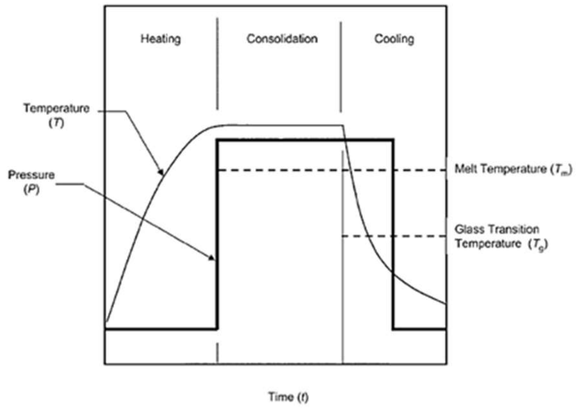


Figure 13.Thermoplastic consolidation

In the last point, the water jet cutting procedure is addressed. We proceeded to manufacture a test piece with a laminate of 6 layers of carbon fiber twill of 3K and 252 gr / m2 of density; and 7 layers of polypropylene film by thermoforming

5.1 Study of the process with mechanical press. Discussion.

Next, the manufacturing procedure and conclusions of the first part of the experiment are described.

With the manual laboratory press, the manufacture of thermoplastic composites has been studied by introducing sequentially fiber and thermoplastic in the form of film or powder.

Regarding the development of the procedure, we start from the general data of "consolidation of thermoplastics" shown in the previous figure "thermoplastic consolidation". 200 x 200 mm specimens will be prepared by inserting powder or film with the fiber, on a flat aluminum mold.

Figure 14.Mechanical press manufacturing laminate scheme

The table below shows the manufactured specimens and the process conditions, indicating for each type of thermoplastic and formulation, the temperatures and closing force of the system. These conditions are related to the characterization of the specimen specifically thickness and fiber content and resin.

Table 4.List of test pieces manufactured in the laboratory with indication of their configuration, production conditions and main characterization parameters

	CONFIGURATION				PROCESS CONDITIONS			CHARACTERISTICS STACK		
Ref.	Carbon fiber	Layers (nº)	Thermoplastic matrix	Format	Temperature (ºC)	Time (min)	Close Force (kg)	Thickness (mm)	Fiber (%)	Resin (%)
# PE1	Twill 200 g/m^2	8	PE	Film	225	15	10	2,0	58	42
# PP1	Twill 200 g/m^2	8	PP	Film	220	15	10	2,0	61	39
# PA1	Twill 200 g/m^2	8	PA	Film	225	15	10	2,0	57	43
# PE2	Twill 200 g/m^2	8	PE	Film	225	15	20	1,7	61	39
# PP2	Twill 200 g/m^2	8	PP	Film	220	15	20	1,7	61	39
# PA2	Twill 200 g/m^2	8	PA	Film	225	15	20	1,7	59	41
# PE3	Twill 200 g/m^2	8	PE	Powder	225	30	10	2,0	53	47
# PP3	Twill 200 g/m^2	8	PP	Powder	220	30	10	2,0	67	33
# PA3	Twill 200 g/m^2	8	PA	Powder	225	30	10	2,0	62	38
# PE4	Twill 200 g/m^2	8	PE WITH 4%TSPE 2102 GAHD	Powder	225	30	10	2,0	53	47
# PE5	Twill 200 g/m^2	8	PE -3% ICORENE3545	Powder	200	30	10	2,0	64	36
# PP4	Twill 200 g/m^2	8	PP with 2% TPPP 9212 GA	Powder	225	30	10	2,0	62	38
# PP5	Twill 200 g/m^2	8	PP - 3% ICORENE4014	Powder	225	30	10	2,0	68	32
# PA4	Twill 200 g/m^2	8	PA6 with 1% TSEB 2113 GB	Powder	225	30	10	2,0	56	44

From the results obtained it can be concluded that film manufacturing is easier to control the homogeneity and the percentage of plastic.

The specimens manufactured from powder did not obtain constant thicknesses, in the tables only the average value is collected representatively, observing in the cross-section microscopy images an irregular plastic content.

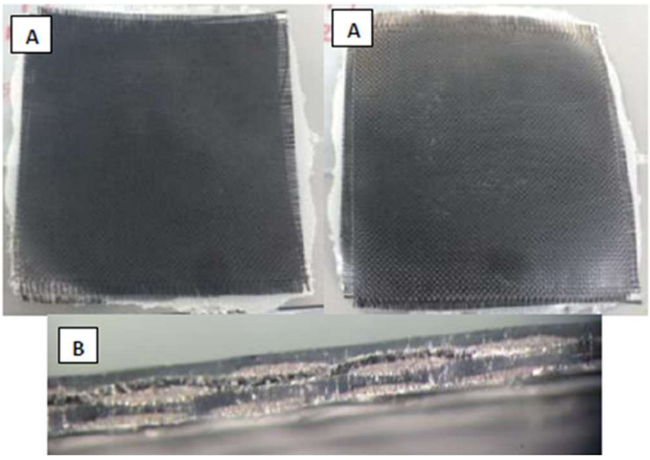


Figure 15.Test sample; Microscopy image, cross section

The procedure followed was with lateral guides that defined the thickness of the thermoplastic layer, and the elimination of excess dust. In order to achieve a homogeneous layer, a grinding cap was made in the plastic shot, selecting in each case the particle size that could be achieved with low-cost industrial grinding processes. Despite controlling the layer thickness and using the smallest particle size possible, good homogeneity results were not achieved. In order to improve the homogeneity, we proceeded to manufacture sheets of a single carbon-matrix layer which were thermoformed one by one.

Finally, from the individual sheets subjected again to a process of temperature and pressure, the composite stack was obtained. In general, with this procedure, better homogeneity results were obtained than those obtained previously. However, the results obtained from the film did not improve, which is why the film was selected for future research, preferably the film

The results obtained show that the production of composites from dust is possible, although it requires special equipment of greater cost. Based on the results obtained, the ideal would be the pulverization of dust on the fibers, this requires not only sprayers or electrospray systems but also control of the application atmosphere.

To obtain a good composite as well as a homogeneity and good compaction, it is desirable to obtain a good fiber-matrix thermoplastic interaction. When we talk about homogeneity in a composite, it is important to evaluate the distribution of plastic matrix between the strands of fiber and to consider the matrix that penetrates the tufts and occupies the interstitial space between the strands that form a strand.

In addition, as can be seen in table 4, modifiers were used to promote viscosity: they can facilitate the penetration of the matrix inside the fiber tufts, improving the properties of the composite while improving the fiber-resin ratio by eliminating more easily surplus plastic matrix.

All these agents besides affecting the rheological properties of the thermoplastic due to its chemical composition and chemical interaction can have an effect interacting with the fibers.

In general, it should be noted that as regards the manufacturing process no appreciable differences were observed using the modified thermoplastic or thermoplastic.

It is important to note that the modifier was introduced in the pellet of the thermoplastic and then subjected to a controlled grinding process to obtain particle size powder 0.4mm maximum. The manufacture of film from the modified pellets is discarded given that for reasons of cost is beyond the scope of this study. Therefore, only the effect was evaluated using powder and not film.

5.2 Optimized process in vertical press 60 Tn. Process parameters for thermoplastic stack manufacture. Mechanical properties

Having studied the obtaining of thermoplastic composites on a laboratory scale, we proceeded to study the manufacturing on an industrial scale. In view of the results, the first key parameter for obtaining thermoplastic composites is to increase and control the pressure exerted on the laminate controlling the amount of thermoplastic matrix in order to obtain a composite of good homogeneous and compact mechanical characteristics.

*NOTE: The objective is to optimize the manufacturing process of thermoplastic composites, implementing low cost solutions that allow a good homogenization of the composite, compact mechanical characteristics and good reproducibility results.

To do this, we proceeded to study the manufacture of thermoplastic composites in a press of 60 tons of 2000 x 1400 mm. of plate with a precision of parallelism between the plates less than 0.25 mm.

Regarding the development of the procedure, panels measuring 300x300 mm with a thickness of 2mm should be prepared, with the idea of being able to extract 10 specimens of dimensions 250x15mm for the performance of tensile tests.

For this, two steel plates must be available, both with a perfectly polished surface.

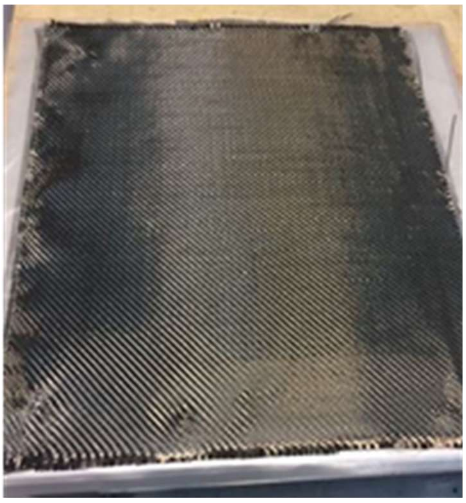


Figure 16.Preparation of carbon fiber material and steel plates

Next, the laminate is placed by inserting the plastic, either powder or film, with the fiber sheets up to a total of 8 sheets of fiber, as indicated in the following scheme:

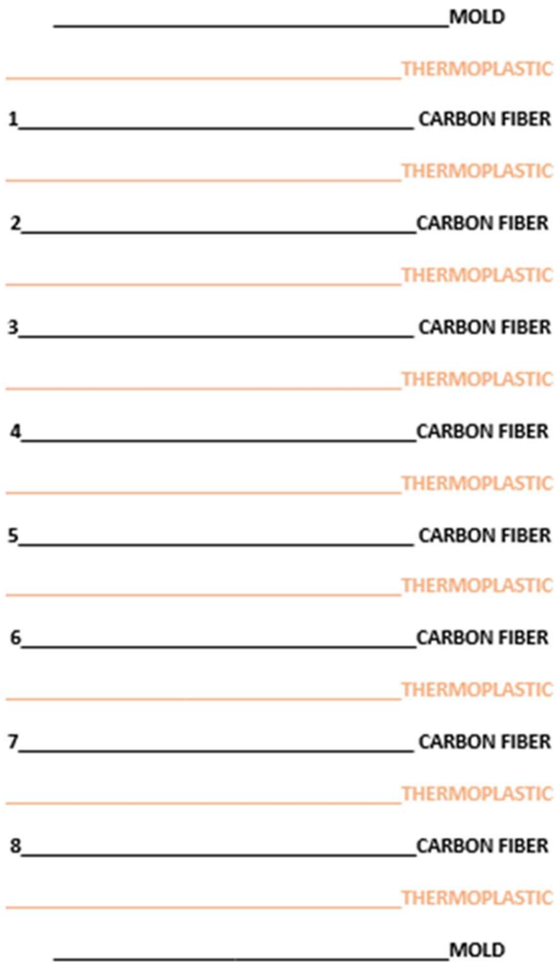


Figure 17.Laminate scheme

The stacking is introduced on the lower plate of the press and the process is started according to the introduced configuration.

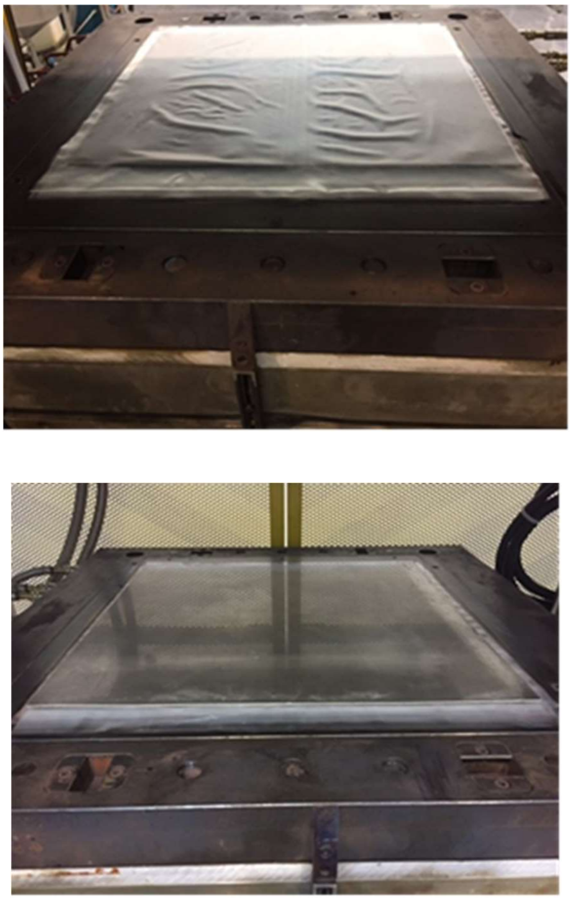


Figure 18.Stack with carbon fiber and thermoplastic; steel plates with the stack into the press

A total of 9 laminates were manufactured, with the process characteristics shown below and the properties obtained were analysed:

Table 5. List of specimens manufactured and tested using the 60 Tn press

Ref.	CONFIGURATION				PROCESS CONDITIONS			STACK PROPERTIES							
	Carbon fiber	Layers (nº)	Thermoplastic matrix	Format	Temperature (ºC)	Time (min)	Close Force (Tn)	Strength		Young modulus		Interlaminar shear		Fiber (%)	Resin (%)
								MPa	SD (Mpa)	MPa	SD (Mpa)	MPa	SD (Mpa)		
# PP1-p	Twill 200 g/m^2	8	PP	Film	220	2	60	474,9	28,7	53387,2	1347,7	199,1	24,4	62	38
# PA1-p	Twill 200 g/m^2	8	PA	Film	225	2	60	460,2	26,5	48841,4	2014,8	170,9	19,1	61	39
# PP3-p	Twill 200 g/m^2	8	PP	Power	220	2	60	374,4	63,4	38345,6	4733,6	-	-	65	35
# PA3-p	Twill 200 g/m^2	8	PA	Power	225	2	60	510,9	24,4	50097,6	1796,0	180,0	16,5	61	39
# PE4-p	Twill 200 g/m^2	8	PE WITH 4%TSPE 2102 GAHD	Power	225	2	60	270,9	9,4	22271,4	41013,6	-	-	59	41
# PE5-p	Twill 200 g/m^2	8	PE -3% ICORENE3545	Power	200	2	60	280,9	51,8	42889,2	5807,4	-	-	65	35
# PP4-p	Twill 200 g/m^2	8	PP with 2% TPPP 9212 GA	Power	225	2	60	421,2	23,6	43781,4	4871,0	209,2	14,8	62	38
# PP5-p	Twill 200 g/m^2	8	PP - 3% ICORENE4014	Power	225	2	60	314,8	44,6	42970,8	5677,0	-	-	65	35
# PA4-p	Twill 200 g/m^2	8	PA6 with 1% TSEB 2113 GB	Power	225	2	60	490,1	24,1	46073,2	1740,3	-	-	60	40

Note: all the stacks were manufactured in a tool providing a 2mm probete

*NOTE: The objective is to optimize the manufacturing process of thermoplastic composites, implementing low cost solutions that allow a good homogenization of the composite, compact mechanical characteristics and good reproducibility results.

** NOTE: Standards of Reference: UNE - EN ISO 527 - 1: 1996 (Plastics. Determination of tensile properties. Part 1: general principles), UNE - EN ISO 527 - 4: 1997 (Plastics. Determination of tensile properties. Part 4: test conditions for isotropic and orthotropic fibre-reinforced plastic composites), UNE - EN ISO 1421: 1998 (Rubber- or plastics-coated fabrics. Determination of tensile strength and elongation at break) and UNE - EN ISO 178: 2003 (Plastics - Determination of flexural properties) standards.

If we observe the results obtained, we can conclude the following aspects:

- In case of PP the best results are obtained from film, whereas in the case of PE the best results are obtained from powder

- In the case of PP, the additive TPPP 9212 GA at 2% improved the resistance properties

- The highest resistance was provided by the PA

- No significant changes were observed in the Young's modulus or in the interlaminar shear of the studied specimens.

Although the studies have been developed in a discontinuous way, the objective is to establish the production conditions that allow later industrialization in continuous. Therefore, the procedure to be studied must be characterized by:

- Be easy to implement with low cost equipment

- Allow continuous production minimizing human participation

- Simplify the stages and productive conditions to achieve low cost processes that, when integrated, involve as little energy consumption as possible.

For this, the first challenge that was established was to develop and evaluate a productive process that does not require the application of vacuum. The application of vacuum in addition to requiring machinery and tooling of higher cost, involves in most situations discontinuous stages and permanence of materials for a longer time in the production stage.

The studied process involves the impregnation of the fibers with the thermoplastic in the form of powder or film, applying a temperature close to the melting of the thermoplastic to reduce its viscosity, increase its fluidity and achieve a greater impregnation of the fibers while applying pressure to achieve the correct impregnation of the fibers and compaction. The pressure must be high enough to decrease the size of the air occlusions.

To evaluate how the pressure reduces air occlusions, uni-directional and biaxial fiberglass specimens with thermosetting resin and manual lamination were fabricated. Once the fabric was impregnated, different pressures were applied to the laminate. Once cured, the simple visualization of the backlit test specimens allows the presence of air to be observed. Pressures on the laminate higher than 6 bar were enough to consider the presence of occlusions negligible.

Based on these results, it was proceeded to manufacture a tool that leaves an exact cavity with the thickness dimensions and apply the maximum closing pressure on the laminate until force closure of tooling. In this way, the necessary layers are piled up to reach the theoretical thicknesses of the tooling and a proportional percentage of thermoplastic is introduced according to the fiber / thermoplastic ratio to be manufactured. It is important that the tooling allows to accommodate the surplus of thermoplastic when pressing while retaining the same surplus to avoid the losses of thermoplastic laminate. This was achieved by controlling the dimensions of the laminate introduced into the mold. So that on the sides of the laminate and inside the cavity the mold is produced thermoplastic accumulation.

Once the quantities of fiber and plastic to be introduced were optimized, the process conditions were studied. For this, the following productive procedure was followed:

- Weight and placement in fiber mold and optimized thermoplastic

- Application of temperature and gradual heating up to the temperature close to the melting point, the increased melting temperature was typically used 4 ° C

- Let the system stabilize for 5 min at the manufacturing temperature

- Application of pressure and closure of the system applying a closing force of 60tn

- Cooling of the system below 50 degrees the melting temperature to cool and proceed to the opening of the system and demolding the stack

This procedure was also applied by preparing the laminate on a cold metal plate and placing the system (plate and laminate) on the hot tooling. In this case the cavity of the tool was increased with the thickness of the laminate support plate and heating was proceeded to proceed with the procedure described above.

5.3 Processes of transformation: thermoforming

Thermoconforming is a fast manufacturing process of thermoplastic composites laminates. Consists of applying a thermoplastic sheet softened by heat and a reinforcement of carbon fiber onto the walls of a mold to shape it.[10]

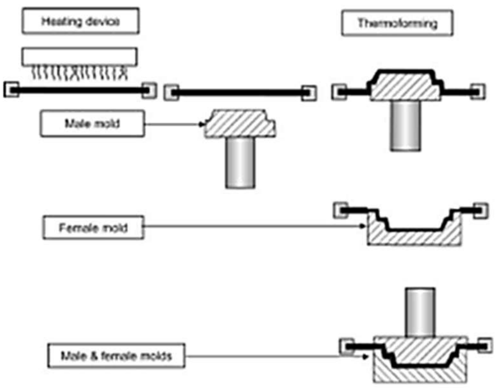


Figure 19.Principle of thermoforming

It is possible to distinguish three fundamental stages of the process, which are:

- Heating of the sample, either by radiation, contact or convection.
- Molding of the sample, which after heating is stretched adapting to the mold by means of different processes (pressure, vacuum, pressure and vacuum or a countermold).

[10] Michel Biron. (2013). *Thermoplastics and Thermoplastic Composites.*

- Cooling of the product, which starts when the composite thermoplastic comes in contact with the mold and is cooled by a fan or at room temperature and ends when the temperature is adequate to unmold the piece without deforming it.

Therefore, the mold can be male, female or in two parts and can take holes for vacuum, air and ventilation.

In this technique of transformation of thermoplastic composites should always take into account a series of parameters, which are:

- Temperature to heat, which depends mainly on the material to be transformed, but also on the complexity and thickness of the piece.
- Heating time, which depends mainly on the thickness of the material, but also on the transmission coefficient thereof. This is very important, and it must be sufficient for the sheet to reach uniformly on the surface and thickness the forming temperature.
- Cooling time, which depends on the same factors as the heating time, and must be sufficient for the finished product to be resistant and not deform when it is demolded.
- Pressure or vacuum, depends mainly on the thickness of the sheet but also on the complexity of the piece. It must be controlled, because if it is insufficient, not all the details will be obtained and if it is excessive, holes or marks may be produced.

Process cycle times are important for large series production of composite parts. It includes the preform manufacturing, the forming stage of the component, trimming when necessary, and assembly of the component into the total (sub)structure.

In a thermoforming process, there are certain basic factors for the design that must be taken into account. Here are briefly listed:

- At the end of the process, after the thermoforming there are always contractions of the piece. The piece will be different from the mold to a greater or lesser degree.

- It must be taken into account that in order to facilitate the demoulding, it must be avoided to design complicated shapes; and with sufficient draft if the material does not allow stretching. Deep holes, cavities and pressings are not controllable; embossing, solid ribs, inserts are not suitable.
- Due to thinning, too small radii of curvature should be avoided, which also damage the impact resistance.

Thermoforming is usually a recommended process in manufacturing processes with a relatively high production rate, compared to more conventional autoclave processes. This is why they are attractive in the automotive and aerospace industry. The low manufacturing cost, ease of handling, good stability, balanced properties and excellent conformability make the use of fabrics very attractive for structural applications in these sectors.

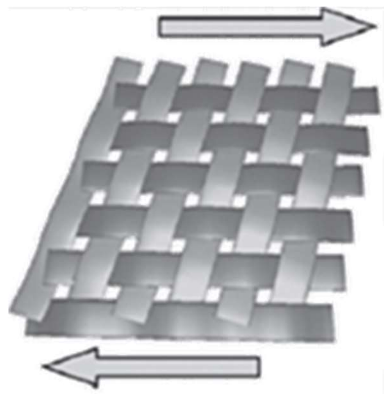
Various deformation mechanisms can be invoked in woven fabric-reinforced composite materials during these forming processes: intraply shear and tensile loading, ply/tool or ply/ply shear, ply bending, and compaction/consolidation.

1. Intraply shear

-Rotation of between parallel tows and at tow crossovers, followed by intertow compaction

-Rate and temperature dependent for prepreg

-Key deformation mode (along with bending) for biaxial reinforcements to form 3D shapes

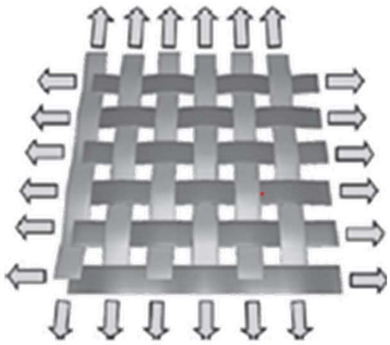


2. Intraply tensile loading

-Extension parallel to tow direction(s)

-For woven material initial stiffness low until tows straighten: biaxial response governed by level of crimp and tow compressibility

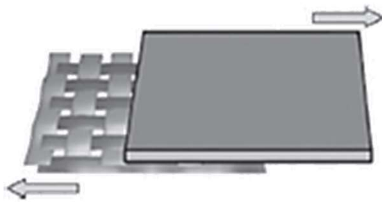
-Accounts for relatively small strains but represents primary source for energy dissipation during forming



3. Ply/tool or ply/ply shear

-Relative movement between individual layers and tools

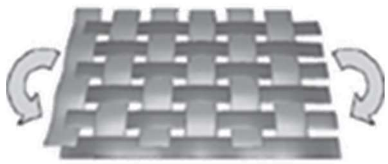
-Not generally possible to define single friction coefficient; behaviour is pressure and (for prepreg) rate and temperature dependent



4. Ply bending

-Bending of individual layers

-Stiffness significantly lower than in plane stiffness as fibres within tows can slide relative to each other, rate and temperature dependent for prepreg

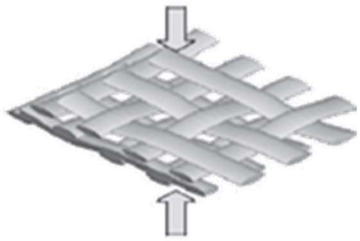


-Only mode required for forming of single curvature and critical requirement for double curvature

5. Compaction/consolidation

-Thickness reduction resulting in increase in fibre volume fraction and (for prepreg) void reduction

-For prepreg behaviour is rate and temperature dependent



With respect to unidirectionally[11] reinforced thermoplastic composites, they provide higher performance (stiffness and specific strength), at least for the properties dominated by the fiber in the plane, possibly with a lower impact performance due to the lack of interlacing.

In the 1980s, manufacturing processes were mainly based on autoclave technology. The double diaphragm shaping is an autoclave forming process enabled with similarities to the thermoforming of unreinforced thermoplastic sheets. The vacuum pressure was only

[11] Michel Biron. (2013). *Thermoplastics and Thermoplastic Composites.*

found to be insufficient for the formation of reinforced laminate. In contrast, a combination of the high pressure and vacuum can be used to form a laminate placed between two thin deformable sheets (the so-called diaphragms). These restrict the deformations of the laminate during the formation and can avoid processing defects, such as wrinkles and cracks.

Although excellent formability can be achieved in this manner, such a (double) diaphragm forming process (Mallon and O'Bra'daigh, 1988; Krebs et al., 1998) does not fully exploit the rapid processing capabilities of thermoplastic composites, as all the configuration must be heated and cooled during each cycle, and assemble a new layer stack for the new cycle is relatively slow.

This drawback is obviously circumvented by press forming preconsolidated laminates as described previously. The only difference is that the plies now have unidirectional (UD) rather than fabric reinforcement. As a first step, exactly the same process chain can be employed: starting with preconsolidated laminates of uniform thickness and stacking sequence, cutting the blank, followed by rapid heating, press forming, consolidation, trimming, and assembly. The forming stage will now induce a different set of deformation mechanisms than observed in fabric reinforcement, as the basic material differs to some extent from fabric-reinforced laminates

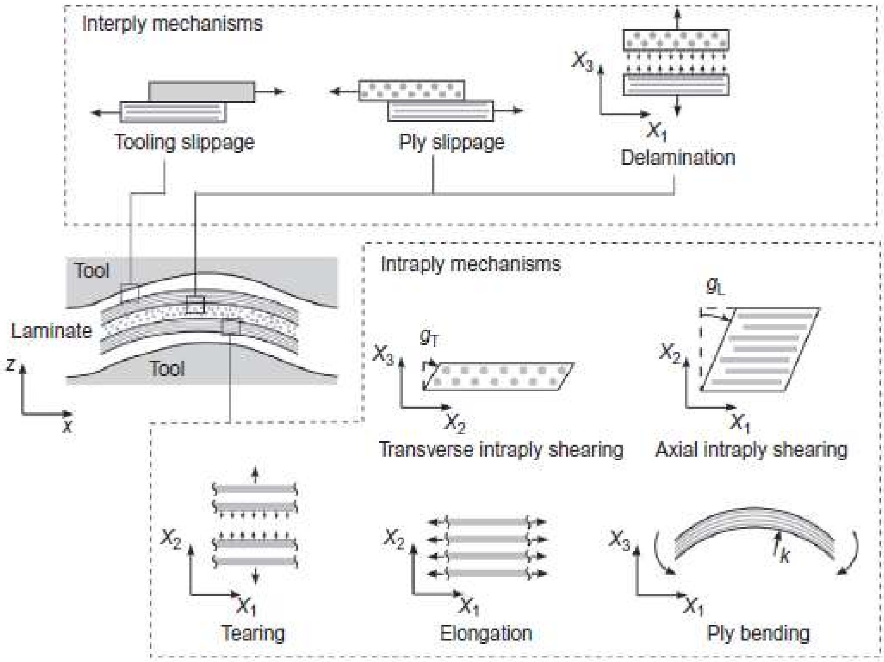


Figure 20.Deformation mechanisms in a laminate with unidirectional reinforcement[12]

5.3.1 Manufacturing and characterization of geometric shapes type

To evaluate what the thermoforming process is like, a twill fabric was selected. That allows to ensure the drapability of each sheet to the geometric shape.

A 90-degree corner, a cylindrical shape and a wavy shape have been defined as type geometric shapes. The mold and countermold with 1 and 2 mm cavities has been built in aluminium. The figure shows a photo of the fabricated tooling.

[12] Michel Biron. (2013). *Thermoplastics and Thermoplastic Composites.*

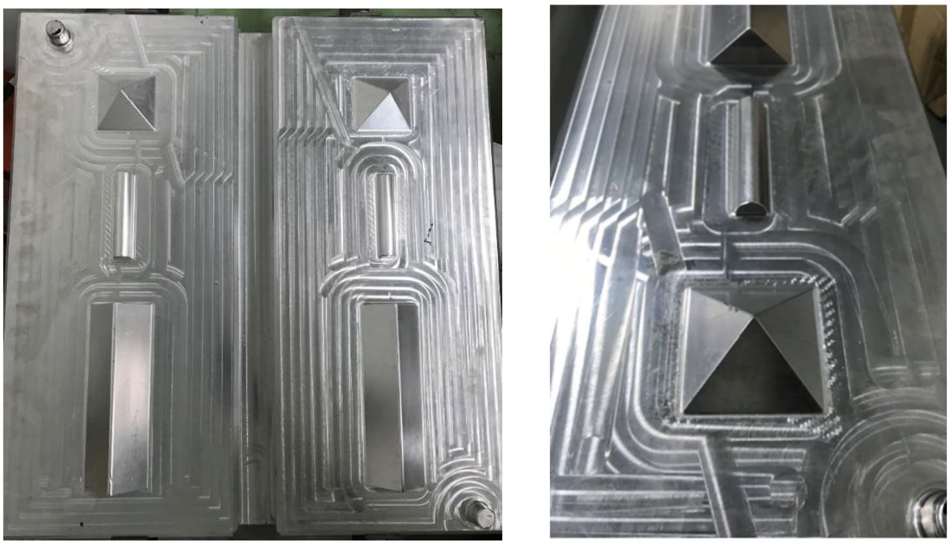


Figure 21. Tooling: A 90-degree corner, a cylindrical shape and a wavy shape

The studies were carried out selecting as thermoplastic matrix polyethylene. For the process it was estimated that a dwell time of 15 min in the IR lamp heating unit, sufficient to reach the optimum temperature of thermoforming, which was defined in 220 degrees

The transfer time of the composite stack from the heating unit to the thermoforming press was lower in all cases to 30 seconds. By using thermocouple probes it has been determined that once outside the IR heating unit, the thermoplastic composite stack takes 4 min to decrease the surface temperature of the stack below 50-55°C, so a transfer time 30 seconds has been considered adequate to ensure that the stack temperature is correct for thermoforming.

In these conditions it has been observed that the stack adapts and is properly thermoconformed in the three forms. In the figure, detail photographs of the thermoformed pieces are shown.

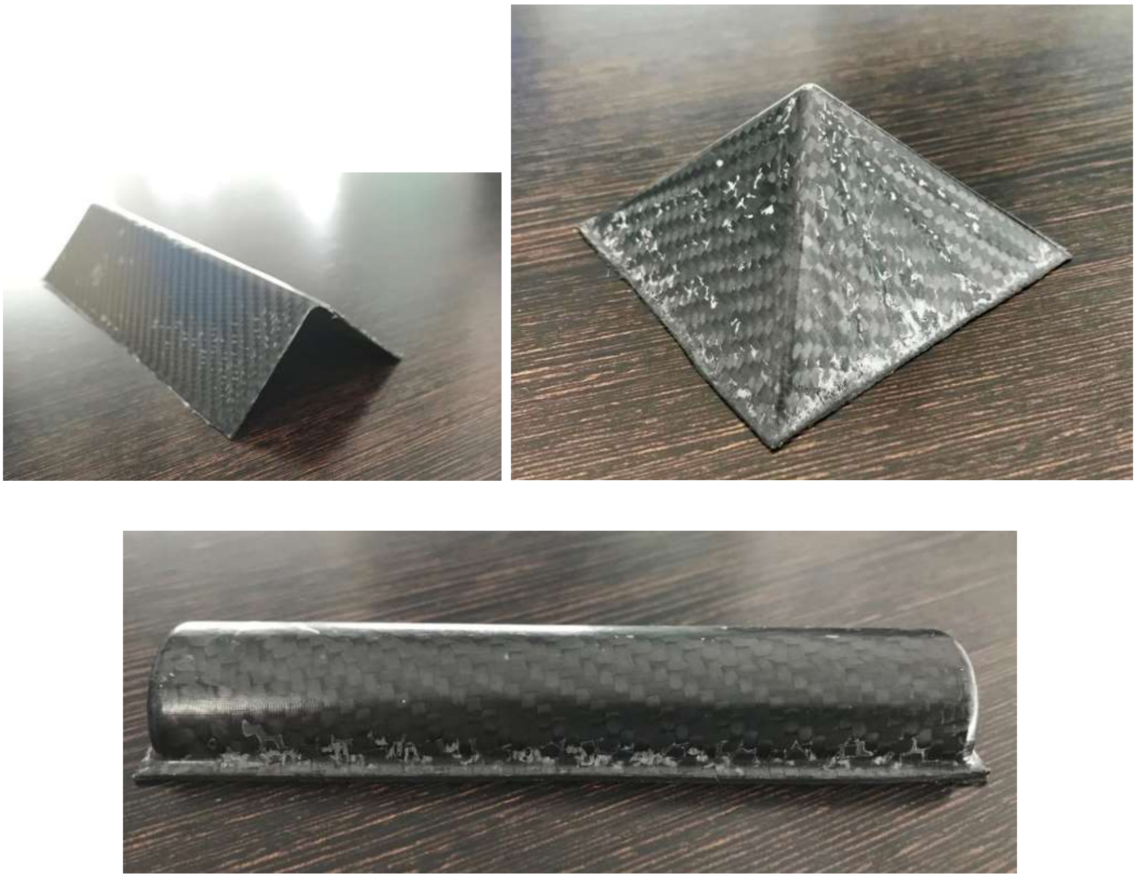


Figure 22.Thermoformed pieces

Based on the results and studies, the following recommendations can be concluded:

- The plastic stack should be heated to the thermoforming temperature and maintained at that temperature for at least 30 s.

- A thermoforming temperature of 30 degrees higher than the melting temperature of the thermoplastic matrix allows to heat the stack of composite with the thicknesses studied 1, 2 and 4 mm without producing plastic matrix drip

- The lateral clamping system of the composite stack must firmly tighten and hold the fibers. And be coupled to a spring that allows deformation of the thermoforming. In our case, tensile springs 30 mm long were used to absorb the dimensional changes

- Clamping tension is an important parameter that defines the final properties and the deformation capacity

- It is critical to ensure through a drapability study that the carbon fabric defined in each sheet can be adapted to the geometric shape, being this drapability study advisable to simulate layer by layer by fiber type

- The clamping strategy used in this study, based on mechanical lateral clamps and springs, is valid for fabrics and multiaxial. For unidirectional fabrics that must be held perpendicular to the direction of the fiber other strategies must be defined

- To ensure rapid transfer between the heating unit and the mold in the press, it is recommended to design quick transfer guides. In this sense, the heating unit has been designed to be placed next to the tool with a system that allows to align the stack to the tool while at the same time it allows to control the distance between the stack and the IR lamps.

- The optimization of the distance of the lamps from IR to the stack is critical to ensure that surface overheating does not occur. At the same time, it must be a suitable heating that allows to reach the optimal temperature inside the stack without producing dripping or loss of thermoplastic matrix. In our studies, good results were obtained by keeping the IR lamps at the thermoforming temperature and at a distance of 40-60 mm from the composite stack. It should be noted that under the selected experimental conditions and with the stack of 1 and 2 mm thickness no drop in thermoplastic matrix has been observed.

- It has been observed that there remain traces of thermoplastic matrix in the lateral clamping claws that hinder the successive execution of processes to avoid it has been protected with this zone the area of subjection with IR refractory blanket so that it is not hot, is an effective strategy not heating the clamping area but has the disadvantage of increasing the clamping area and material disposal.

- The minimum distance between the clamping area and the useful part area is at least 20-30 mm. With the tests performed it is noted that it is difficult to decrease this area. This does not present a major problem since it is of the same order of magnitude as the surpluses that are left in other productive processes even of thermostable matrix.

5.4 Procedure for cutting thermoplastic composites. Water jet

In order to define and limit the cutting parameters by water jet with abrasive that offer a quality result, we are going to perform cutting tests of a test piece.

The test piece has been manufactured by thermoforming with a laminated of 6 layers of carbon fiber twill of 3K and 252 gr / m2 of density; and 7 layers of polypropylene film.

The water cut is achieved by a jet of water at ultra-high pressure. An ultra-high-pressure pump generates a water flow with nominal pressures reaching 6000 bar. The process resides in the ability of the equipment to expel water, through a hole of very small diameter (varies from 0.1 to 0.5 mm) with enough pressure to cut the material. This creates a very thin flow at high speed. Next, the water jet is mixed in a mixing chamber with an abrasive (garnet sand), which acquires the speed of the water. Finally, the water is projected through a nozzle to make the cut in the material. The jet of water at the outlet of the nozzle reaches an ultrasonic speed of around 1000 m / s. In the case to be studied, we will vary the speeds between 75 m / s to 1800 m / s. The nozzle or mixing tube is made of tungsten carbide, a hard and resistant material to resist erosion.

The general process described and the outline of the “head” assembly are shown below:

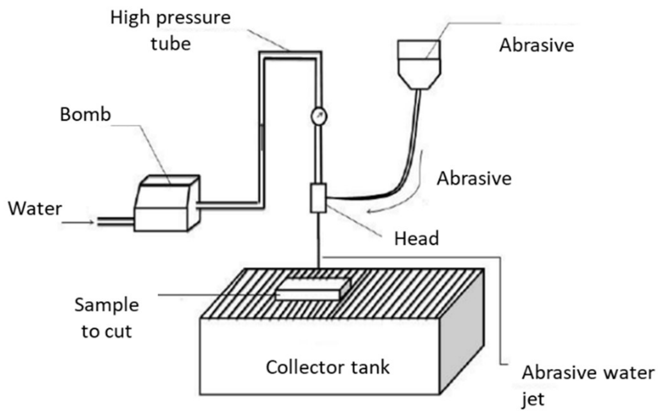


Figure 23.Process to cut of thermoplastic by water jet

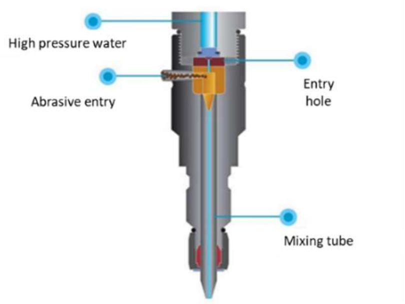


Figure 24. Head assembly

For the realization of the essay have combined three variables: speed of cut, pressure and amount of abrasive:

SPEED OF CUT (m/sg)	75 – 150 – 300 – 600 – 900 – 1800
PRESSURE (bar)	1000 – 1500 – 2500 – 3500
AMOUNT OF ABRASIVE (gr/min)	0 – 100 – 150 – 250 - 300

Table 6. Variables water jet process

To carry out the test, the different variables will be combined so that, for a constant pressure, different cuts are made for certain concentrations of abrasive and variable speed, as shown in the following scheme:

CONSTANT PRESSURE	ABRASIVE 0	PROOF OF 6 CUT WITH WATER JET VARIING THE SPEED FROM 75 TO 1800 
	ABRASIVE 100	
	ABRASIVE 150	
	ABRASIVE 250	
	ABRASIVE 300	

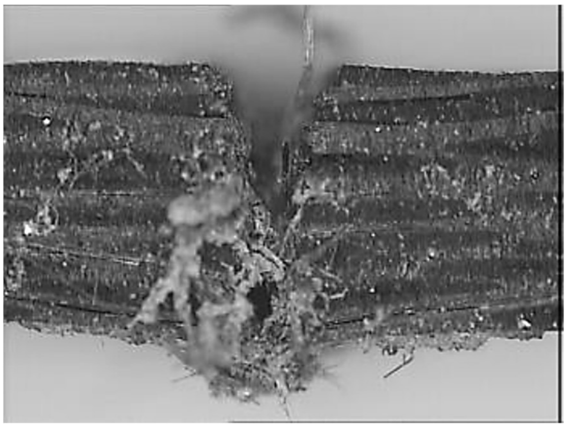
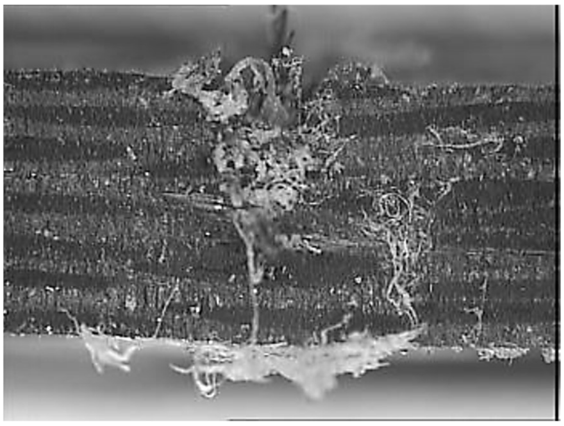
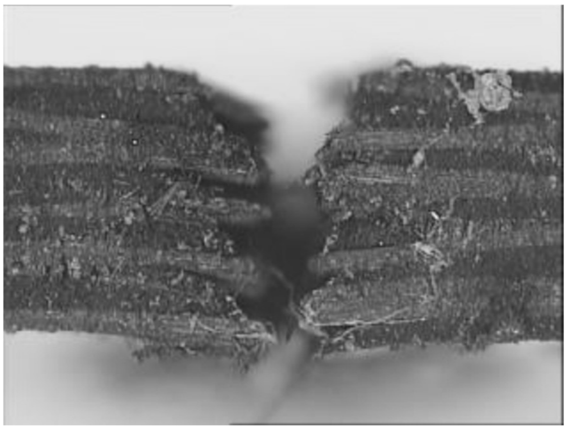
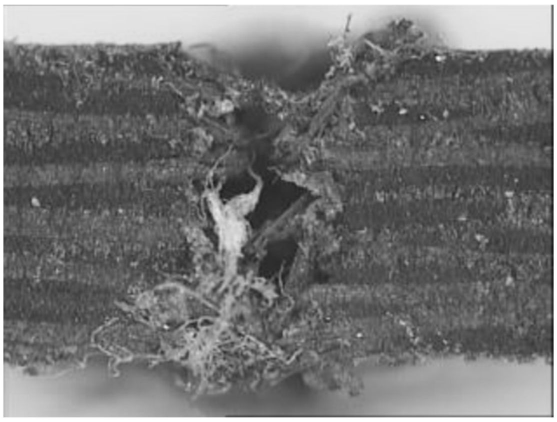
Table 7.Combination of variables water jet process

Finally, we have obtained 4 samples according to the pressures studied: 1000, 1500, 2500, 3500. From them, the rugosity and tapper produced have been evaluated, as well as an inspection by macrographs of the possible internal delamination.

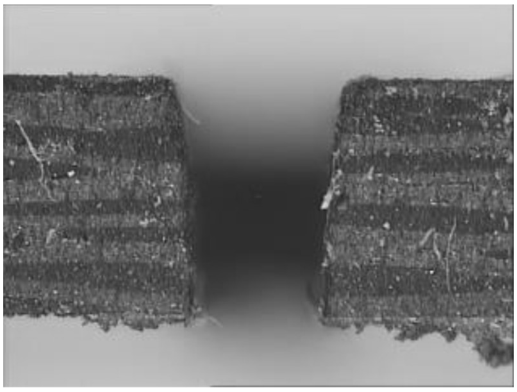
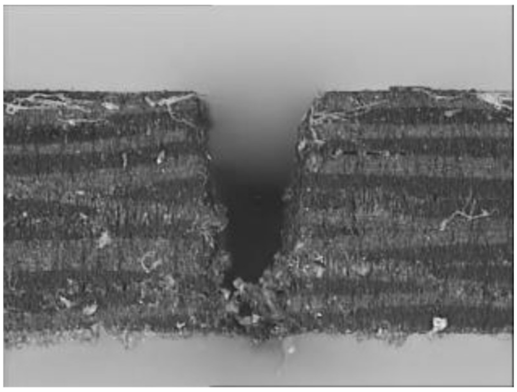
Figure 25.Samples obtained to realize water jet process

After analysing the cuts of the previous image one by one, basically the following conclusions can be drawn:

1. The greater the application of pressure and the lower the speed, the percentage of delamination decreases. Below, two images are shown for comparison.

Pressure: 1000 bar V: 75 m/s Abrasive: 0 gr 	Pressure: 1000 bar V: 1800 m/s Abrasive: 0 gr 
Pressure: 3500 bar V: 75 m/s Abrasive: 0 gr 	Pressure: 3500 bar V: 1800 m/s Abrasive: 0 gr 

2. Kerf Taper: Factor where it is observed that the width of the cut varies along the cut from top to bottom. This difference in width is usually called the conical shape of the cut. This factor can be positive or negative, that is, the width in the lower form of the cut can be larger or smaller than in the width in the upper part. It is observed that at higher speed greater conical effect. However, as we increase the pressure, this effect decreases.

Pressure: 1000 bar V: 150 m/s Abrasive: 150 gr 	Pressure: 1000 bar V: 1800 m/s Abrasive: 150 gr 

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May 2019
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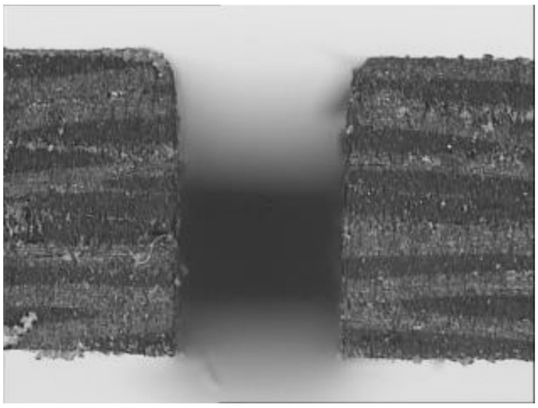
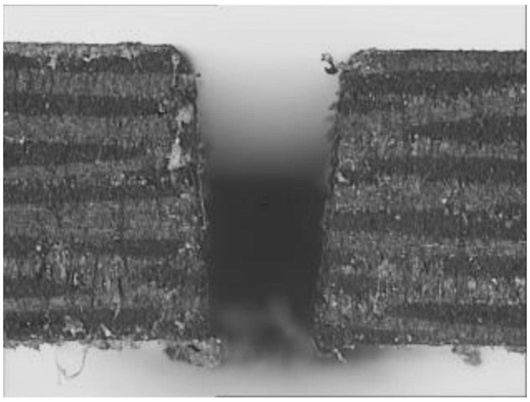
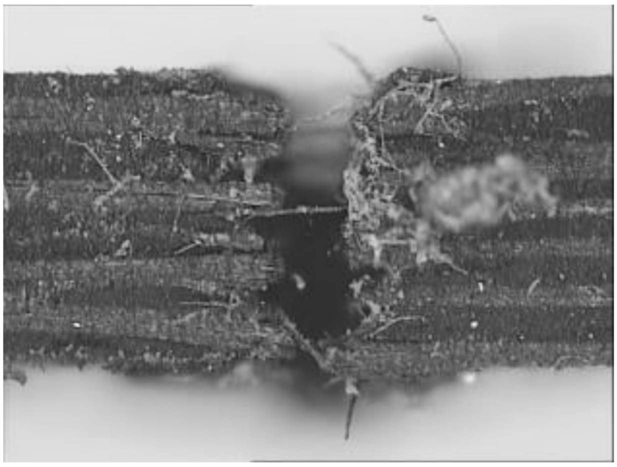
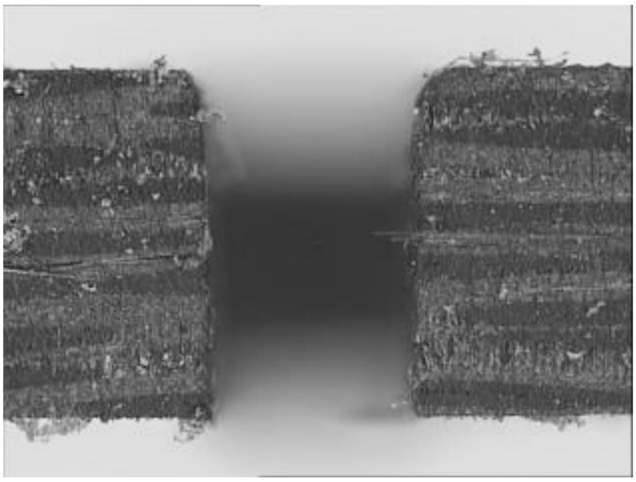
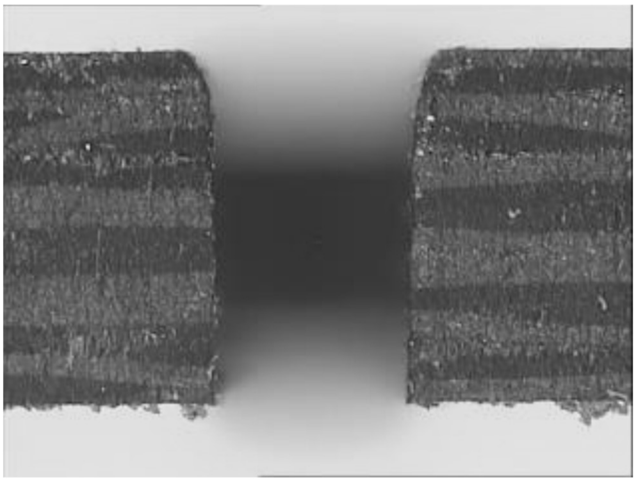
Pressure: 3500 bar V: 150 m/s Abrasive: 150 gr *(next pg →)* 	Pressure: 3500 bar V: 1800 m/s Abrasive: 150 gr *(next pg →)* 

3. Finally, another factor clearly observed is that, the greater the amount of load, a cleaner cut is observed with no burrs.

	Pressure: 2500 bar V: 75 m/s Abrasive: 0 gr
	Pressure: 2500 bar V: 75 m/s Abrasive: 150 gr

	Pressure: 2500 bar V: 75 m/s Abrasive: 300 gr

6. GENERAL DISCUSSION: POTENTIAL AND LIMITATION OF THERMOPLASTIC COMPOSITES

For reasons of profitability and technical development, composites with thermosetting matrices have been used more than composites with thermoplastic matrices. Its excellent fluidity facilitates the penetration of the resin and consequently, the degree of impregnation of the fiber, its processing being easier.

This means that in terms of market, the elements manufactured with thermostable matrices are more demanded and fit in terms of quality and cost.

Even so, it has to be admitted that thermostable composites present some weak points that in thermoplastics are presented as strengths. For example, they have greater resistance to impact and fire, reduce the phenomenon of moisture absorption, improve resistance to certain chemical agents.

Regarding processing, thermoplastic composites have shorter manufacturing cycles, which implies the relevant reduction in cost if the production rate is high enough. In addition, regarding the raw material itself, it is worth highlighting the possibility of storage without restrictive conditions and its recyclability.

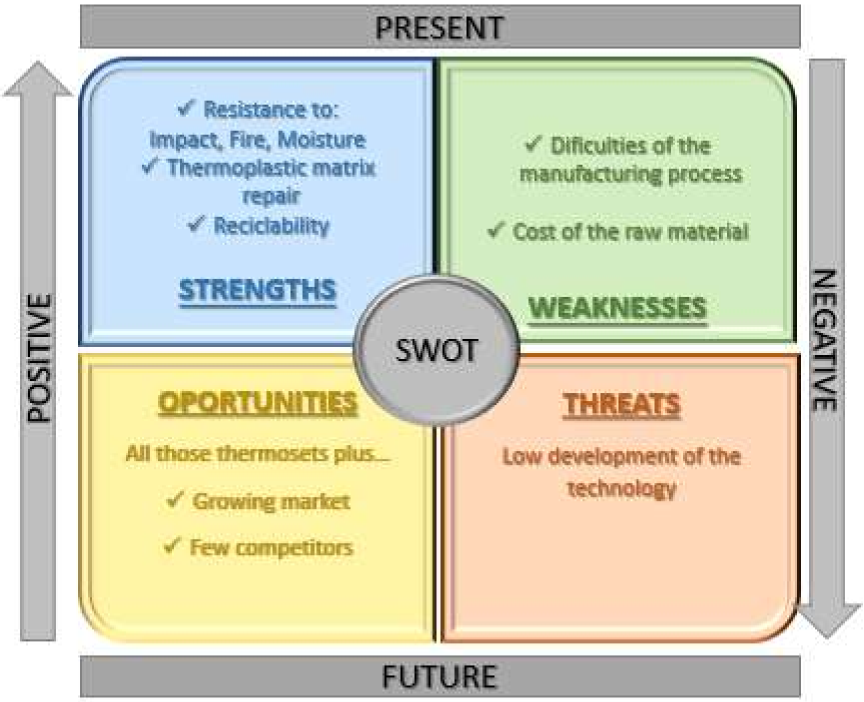


Figure 26.SWOT Matrix

In sectors such as aeronautics, where manufacturing processes are expensive; and the construction sector, where deployment in infrastructure is very heavy, it is important to develop techniques that facilitate the repair of composite elements. Thermoplastics have the ability to be repaired using welding with heat and pressure (fusion bonding), a short process of duration and easy to implement with portable equipment, which makes it interesting in these sectors, therefore, another point to favour of these matrices.

In spite of the mentioned goodnesses, one still has to continue advancing in improving and optimizing the manufacturing technology with thermoplastic composites and overcoming difficulties given by their physical properties. In short, we have a product with exceptional properties, a market in which competition is limited, although highly specialized, and a field of application that has been growing since the last few years, and is becoming wider. We have in our hands the improvement of the composites industry and we could even say “reinvent the fiber”.

7. GENERAL CONCLUSIONS

- It is possible to industrialize at low cost the stack production of thermoplastic composite from film and dry fiber, being sufficient to control temperature and pressure. With the correct control of pressure, temperature and process time it has been possible to manufacture functional stack without the need to apply vacuum

- It is necessary or advisable to incorporate additives to increase the matrix-fiber interaction and improve the properties of the composite.

- The use of additives influences in an improvement of the thermoplastic processing, but it is necessary to carry out a previous economic analysis to avoid extra costs due to the use of the additive itself or the acquisition of equipment or tools for dispersion and homogenization thereof.

- Low cost and low melting point plastics such as PP, PE, PA6 allow to obtain composites with interesting properties in combination with carbon fiber. They can also be easily thermoformed to obtain pieces of defined geometry.

- The trimming of the thermoplastic composites can be easily carried out with water jet, making it possible to optimize the process conditions to obtain straight and clean cuts without causing dislocations. It is an easy technology to apply and implement in high-speed productions.

- There are several manufacturing processes for thermoplastic composites, but the operating principles of the thermoforming process make it a traditional method from a conceptual point of view.

- Both polyamide and polypropylene have a high interlaminar resistance compared to thermosetting resins, which makes them ideal for working against impacts or accidental knocks.

In short, we are on the path to improving composites and thermoplastic composites are an alternative. No engineer or designer can ignore plastics, but the decision to use a new material is difficult and important at the same time. It has both technical and economic consequences. At present, premises such as market demand, the ability to adapt both technically and economically, the ability to innovate and, above all, the so-called point of "respect for the environment" and "recyclability" will mark the consumption of thermoplastic composite materials

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