POLITECNICO DI MILANO
School of Industrial and Information Engineering
Department of Chemistry, Materials and Chemical Engineering “Giulio Natta”
Master of Science in Materials Engineering and Nanotechnology

# “DEVELOPMENT AND CHARACTERIZATION OF GLASS FIBER REINFORCED POLYMER COMPOSITES FROM RECYCLE WIND TURBINE WASTE”.

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# Glossary

**D**

| | |
|---|---|
| DSC | Differential Scanning Calorimetry |

**E**

| | |
|---|---|
| EoL | End-of-Life |

**G**

| | |
|---|---|
| GFRP | Glass Fibre Reinforced Polymer |

**P**

| | |
|---|---|
| PMMA | Polymethyl Methacrylate |

**S**

| | |
|---|---|
| SEM | Scanning Electron Microscopy |

**T**

| | |
|---|---|
| Tg | Glass Transition Temperature |

**U**

| | |
|---|---|
| UV-DSC | Ultraviolet Differential Scanning Calorimetry |

# Abstract

As the world population grows exponentially, consumption rates and demand for new products also increase dramatically. As a result, a large number of end-of-life (EoL) products are continuously being phased out, resulting in a number of environmental problems.

This Final Master's Degree Project aims to perform the development and characterisation of fibreglass reinforced polymer composites from the recycling of wind turbine waste, specifically through the mechanical recycling of the blades of EoL wind turbines.

This thesis is part of the initiatives belonging to the Europe 2020 strategy to generate sustainable, intelligent and inclusive growth, that is, a Europe that uses resources efficiently. The thesis work was performed in the framework of a Horizon 2020 European project entitled “FiberEUse, Large scale demonstration of new circular economy value-chains based on the reuse of end-of-life fibre reinforced composites” (Project Number 730323). Therefore, the final objective of this thesis is the manufacture of a new composite material for subsequent applications, achieving the principle of Circular Economy to EoL compounds.

First, samples of glass-fibre reinforced polymer composites were prepared. The composites were made from 60% by weight of recycled glass fibres together with the commercial epoxy resin AralditeBY158 and the commercial reagent Aradur21 which modifies the viscosity and gelling time of the resin, since according to previous studies the optimal amount of recycled glass fibres was 60% by weight. These material samples were characterized through different properties such as tensile strength, glass transition temperature, contact angle measurements by sessile drop method among others.

Finally, thanks to the positive results obtained from the composite material, the surface of the material was coated to optimize its properties. Different types of commercial reagents such as Omnicat440, succinic anhydride and phthalic anhydride and different technologies for the deposition of coating solutions such as airbrush and brush will be used. Especially the method of curing with UV light was employed. The best coating results were obtained with a plasma pre-treatment technology of the surface of the composite prior to the coating stage and by using the airbrush for the deposition of the coating solutions.

However, due to the current situation caused by the Covid-19 virus it has not been possible to obtain an optimal coating solution for the surface finishing of the remanufactured material.

In order to carry out this work, several characterization techniques have been used, such as differential scanning calorimetry (DSC) and UV-DSC, tensile tests and contact angle measurements.

# Estratto in lingua italiana

Con la crescita esponenziale della popolazione mondiale, anche i tassi di consumo e la domanda di nuovi prodotti aumentano drasticamente. Di conseguenza, un gran numero di prodotti a fine vita (EoL) vengono continuamente eliminati, causando una serie di problemi ambientali.

Questo progetto di Master Finale mira a realizzare lo sviluppo e la caratterizzazione di compositi polimerici rinforzati con fibra di vetro provenienti dal riciclaggio dei rifiuti delle turbine eoliche, in particolare attraverso il riciclaggio meccanico delle pale delle turbine eoliche EoL.

Questa tesi fa parte delle iniziative della strategia Europa 2020 per generare una crescita sostenibile, intelligente e inclusiva, cioè un'Europa che usa le risorse in modo efficiente. Il lavoro di tesi è stato svolto nell'ambito di un progetto europeo Horizon 2020 intitolato "FiberEUse, Dimostrazione su larga scala di nuove catene del valore dell'economia circolare basata sul riutilizzo di compositi rinforzati con fibre a fine vita" (progetto numero 730323). Pertanto, l'obiettivo finale di questa tesi è la produzione di un nuovo materiale composito per le applicazioni successive, raggiungendo il principio dell'economia circolare ai composti EoL.

In primo luogo, sono stati preparati campioni di compositi polimerici rinforzati con fibre di vetro. I compositi sono stati realizzati con il 60% in peso di fibre di vetro riciclate insieme alla resina epossidica commerciale AralditeBY158 e al reagente commerciale Aradur21 che modifica la viscosità e il tempo di gelificazione della resina, poiché secondo studi precedenti la quantità ottimale di fibre di vetro riciclate era del 60% in peso. Questi campioni di materiale sono stati caratterizzati attraverso diverse proprietà come la resistenza alla trazione, la temperatura di transizione vetrosa, le misurazioni dell'angolo di contatto con il metodo della goccia sessile, tra le altre.

Infine, grazie ai risultati positivi ottenuti dal materiale composito, la superficie del materiale è stata rivestita per ottimizzarne le proprietà. Saranno utilizzati diversi tipi di reagenti commerciali come l'Omnicat440, l'anidride succinica e l'anidride ftalica e diverse tecnologie per la deposizione di soluzioni di rivestimento come l'aerografo e il pennello. In particolare è stato utilizzato il metodo di polimerizzazione con luce UV. I migliori risultati di rivestimento sono stati ottenuti con una tecnologia di pretrattamento al plasma della superficie del composito prima della fase di rivestimento e utilizzando l'aerografo per la deposizione delle soluzioni di rivestimento.

Tuttavia, a causa della situazione attuale causata dal virus Covid-19 non è stato possibile ottenere una soluzione di rivestimento ottimale per la finitura superficiale del materiale rigenerato.

Per eseguire questo lavoro sono state utilizzate diverse tecniche di caratterizzazione, come la calorimetria a scansione differenziale (DSC) e UV-DSC, prove di trazione e misure dell'angolo di contatto.

# 1. INTRODUCTION

## 1.1. Background

Throughout history, the relationship between humans and nature has changed. At first, the capacity of human beings to alter the planet was punctual and limited, but in recent years their uncontrolled activity has led to the degradation of the environment, putting the entire planet at risk.

One of the most widely used measurement techniques to confirm this is our ecological footprint, closely related to global sustainability by determining the consequences of our behaviour with the planet [1].

For this reason, today, in order to contribute to the growth of modern society in a sustainable way, the promotion of development and management of an optimal life cycle in the different technological fields is of great importance. In other words, any technology must be considered from its origin to the end of its life, taking into account its entire period of development.[2] Here it comes, the popular concept of circular economy.

To achieve this prospective, the project based on the reuse of waste from the wind sector, such as the blades of disused wind turbines was born and developed.

## 1.2. Circular economy

The circular economy is an economic concept that is interlinked with sustainability, and whose aim is to keep the value of products, materials and resources in the economy for as long as possible, and to minimise the generation of waste. It is a question of implementing a new economy, circular -non-linear-, based on the principle of "closing the life cycle" of products, services, waste, materials, water and energy.

This desire to bring about a circular economy in society arises as a result of implementing one of the initiatives belonging to the Europe 2020 strategy, to generate sustainable, intelligent and inclusive growth, in other words, a Europe that uses resources efficiently.

A scheme of the circular economy [3] is shown in Figure 1.

*Figure 1. Scheme of the circular economy.*

This initiative is intended, among other things, to help:

- Create new opportunities for economic growth by promoting innovation and competitiveness.
- Ensure the security of primary resources.
- Support the fight against climate change by limiting the use of resources.
- Increase the economy by improving economic performance while decreasing the use of resources.

Achieving a circular economy requires the intersection of social, economic and environmental aspects.

The basic principles on which the circular economy is based are as follows:

- Eco-conception: considers the environmental impacts throughout the life cycle of a product and integrates them from its conception.
- Industrial and territorial ecology: establishment of a mode of industrial organisation in the same territory characterised by optimised management of stocks and flows of materials, energy and services.
- The economy of "functionality": privileging use over possession, the sale of a service over a good.
- The second use: reintroducing into the economic circuit those products that no longer correspond to the initial needs of consumers.
- Reuse: to reuse certain waste or parts of waste, which can still be used to make new products.
- Repair: finding a second life for damaged products.
- Recycling: taking advantage of the materials found in the waste.
- Recovery: to make use of energy from waste that cannot be recycled.

As we have commented previously, the concept of circular economy arises as a consequence of our economy whose system is linear has reached its limits causing that fossil fuels and natural resources on which we depend begin to run out.

Therefore, in order to rectify and improve our relationship with the planet, the circular economy proposes a new model of society that uses and optimizes the stocks and flows of materials, energy and waste in addition to the efficiency of resource use.

In short, the primary objective of the circular economy is that the waste of some becomes a resource for others. Therefore, the manufactured product must be designed so that it can be deconstructed for reuse.

The benefits of developing a circular economy would be to decrease the use of resources, reduce the production of waste and limit energy consumption. In addition to the environmental benefits, this emerging activity is creating wealth and employment throughout the territory and its development should allow for a competitive advantage in the context of globalization.

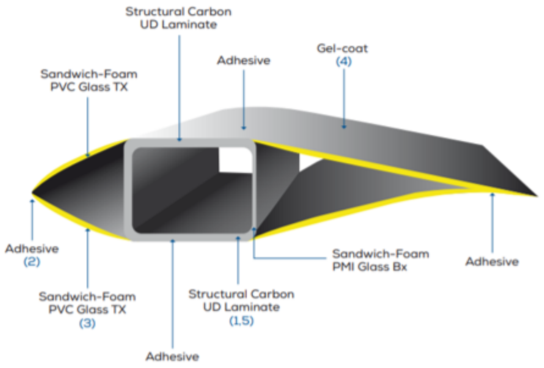
## 1.3. Wind energy

Wind energy, as we already know, is one of the most developed renewable energies. It generates electricity through the force of the wind, by using the kinetic energy produced by the effect of air currents. Therefore, it is a clean and inexhaustible source of energy, which reduces the emission of greenhouse gases while preserving the environment [4].

Wind energy produces energy through wind turbines thanks to the movement of a propeller that, through a mechanical system, turns the rotor of a generator that produces electrical energy. These turbines are usually grouped into concentrations called wind farms in order to achieve a better use of energy, reducing its environmental impact.

Today, the European Union moves towards a circular economy. Therefore, the goal of the wind industry is to make its turbines 100% recyclable since most of the components of a wind turbine (the base, the tower, the gearbox components and the generator) are recyclable [5].

However, achieving 100% recycling is not being so easy because the turbine blades represent a great challenge. These are made of composite materials which allows us to manufacture them in a lighter and more elongated shape. In Figure 2 we can appreciate a generic composition of a turbine blade.



1) **Reinforced fibres** (glass, carbon, aramid or basalt)
2) **A polymer matrix** (thermosets such as epoxies, polyesters, vinyl esters, polyurethane, or thermoplastics)
3) **A sandwich core** (balsa wood or foams such as polyvinyl PVC, PET)
4) **Coatings** (PE, PUR)
5) **Metals** (copper wiring, steel bolts, etc.).

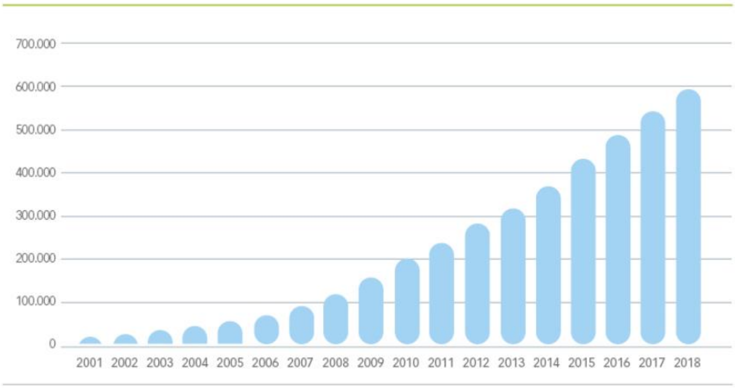
*Figure 2. Generic composition of a wind turbine blade.*

However, the complexity of these composite materials requires specific processes for recycling. For this reason and in particular, one of the main concerns of the wind industry is to contribute to the development of a circular economy through the re-use of its waste such as the blades of disused wind turbines (Figure 3) [3]. It is in this context that this project arises and is developed: to reuse the material from disused blades for the manufacture of new composite materials.

*Figure 3. Scheme of the life circle of a wind turbine blade.*

The main reason to be aware of achieving a circular economy is because the implementation of wind energy is growing in the world.

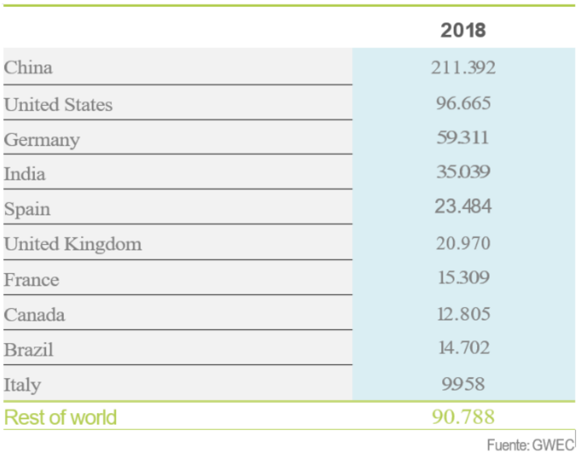
For example, in 2018, the installed capacity was 591,000 MW, according to the Global Wind Energy Council (GWEC) (Figure 4).



Fuente: GWEC

*Figure 4. Evolution of the installed power in the world (in MW) in 2018.*

In Figure 5 we can see that the world's leading producers in 2018 were China, the United States, Germany, India and Spain.



| | 2018 |
|---|---|
| China | 211.392 |
| United States | 96.665 |
| Germany | 59.311 |
| India | 35.039 |
| Spain | 23.484 |
| United Kingdom | 20.970 |
| France | 15.309 |
| Canada | 12.805 |
| Brazil | 14.702 |
| Italy | 9958 |
| Rest of world | 90.788 |

Fuente: GWEC

*Figure 5. Ranking of countries by accumulated installed power in MW.*

In spite of this, the wind energy industry is considered to be one of the industries that produces less composite waste ahead of the construction sector, the electrical and electronic sector, transportation and marine sector in addition to producing clean energy.

### 1.3.1. Outlook to 2020 and 2030

According to the publications in the WindEurope reports "Perspectives for 2020" and "Scenarios for 2030", wind energy will have the potential to provide up to 30% of Europe's energy by 2030, reaching a total of 323 GW, 253 GW onshore and 70 GW offshore as shown in Figure 6.

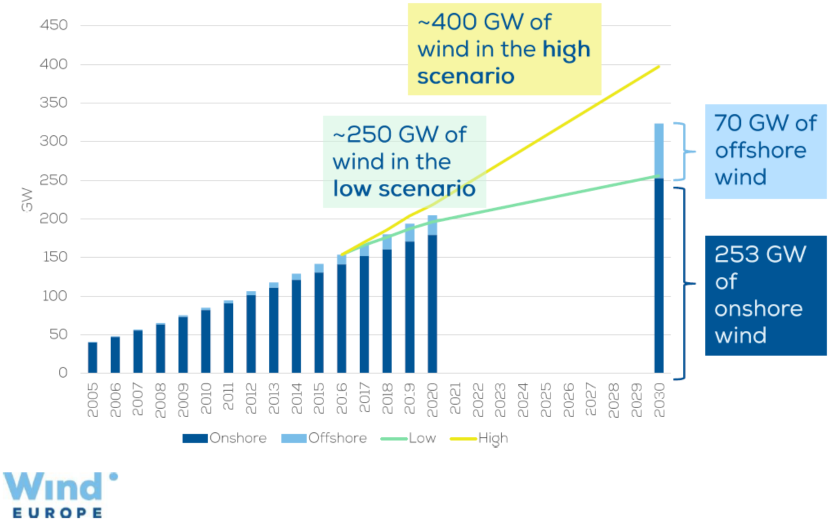


*Figure 6. Cumulative installations by 2030.*

Achieving this prediction will be possible if the right policies are implemented and significant changes are made to the energy system through binding and ambitious energy and climate action plans that deliver a good result on clean energy determined at EU-level.

In fact, in 2016 the European Commission presented the Clean Energy for All Europe legislative package, outlining the post-2020 EU regulatory framework for renewable energy, the internal energy market, security of supply and energy efficiency which sets out the basic rules that will shape the deployment of wind energy until 2030, including a series of measures to ensure the investments needed to meet the EU's binding target for renewable energy.

According to the central scenario in the EU in 2030, the prediction of wind energy installed capacity by country appears in the following Figure 7.

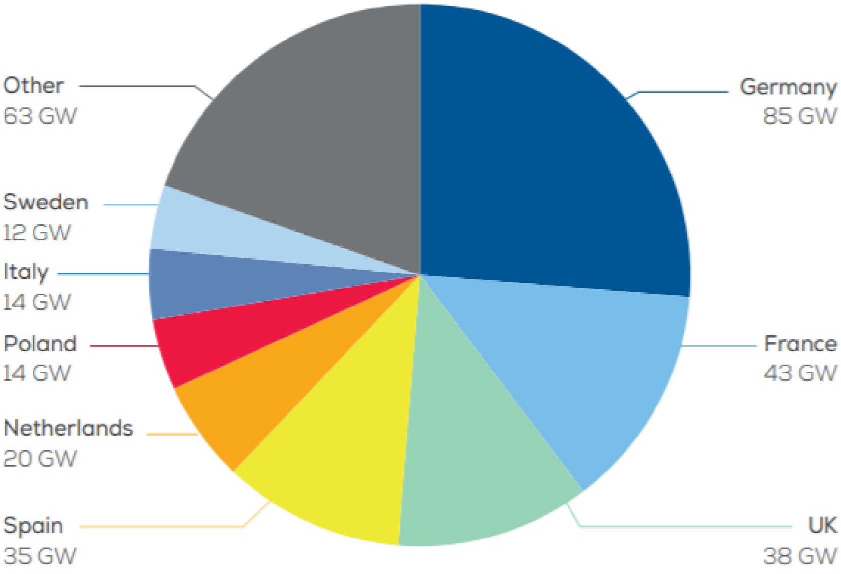


*Figure 7. Provision of 2030 wind energy installed capacity by country.*

Germany, France and the UK would have the largest installed capacity, with 85 GW, 43 GW and 38 GW respectively. France would overtake the UK and Spain in second place thanks to the policies implemented by the new government. Meanwhile, Denmark, Ireland, Estonia and the Netherlands would form an exclusive club of countries that would get more than 50% of their electricity from wind by 2030.

This growth in the wind sector would mean a reduction of up to 382 tonnes of CO2 emissions annually as well as avoiding imports of fossil fuels and an increase in employment.

## 1.4. Composite materials

This section will discuss specifically about the world of composite materials as well as their main characteristics, types and manufacturing and recycling.

### 1.4.1. Definition of composite material

Today, many industries and applications have the need to find new materials with a number of particular properties that are difficult to find in traditional materials.

For this reason, the need arose to manufacture composite materials, i.e. to create a new material whose set of properties at the macroscopic level is superior to that of its initial components of different nature separately. The result would therefore be a multiphase material that retains a significant proportion of the properties of the constituent phases so that it presents the best possible combination.

Composite materials consist of one or more dispersed phases, called reinforcements, distributed within a continuous phase called a matrix (Figure 8). The main function of the matrix is to maintain the proper bonding of the material and to promote a good transmission of forces from the matrix to the reinforcement of the material. This transmission of forces depends mainly on the quality of the interface or contact zone between the reinforcement and the matrix.[6]

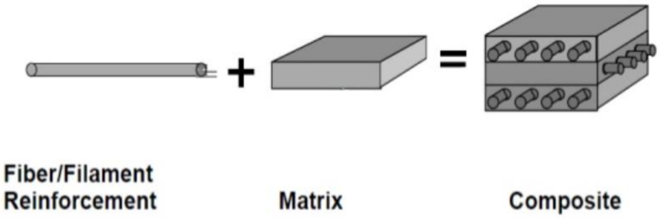


*Figure 8. Composition of composite.*

In the following Figure 9 we can see a general scheme of the types of matrixes and reinforcements in composite materials.

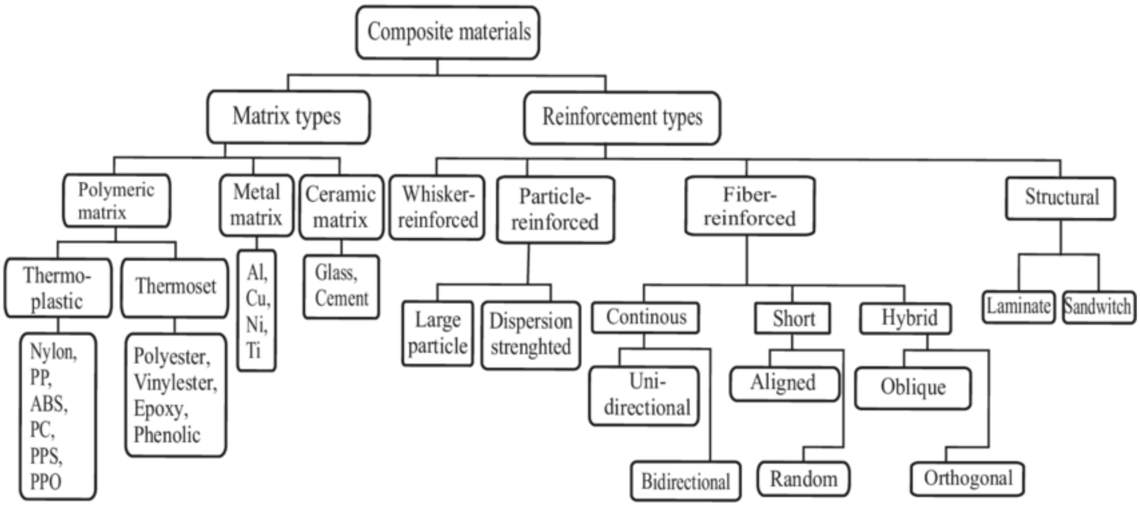


*Figure 9. General classification of Composite materials.*

When designing a composite material, it is essential to take into account the nature and properties of both the matrix and the reinforcement, the geometry, size, orientation, concentration and arrangement of the reinforcement in the matrix and the bonding at the interface of both constituents.[7]

One of the great benefits of composite materials is the obtaining of materials with high mechanical performance as well as being lightweight materials that replace metallic materials in many applications.

As human needs and demanding technological solutions increase, the need for new materials that offer ever better performance increases too.

Thus, for engineering applications, the need arises to obtain new materials, which we will generically call composite materials, which are capable of combining the properties that ceramic materials, plastics and metals have at the same time.

In Figure 10 we can see how the main materials have evolved over the years [8].

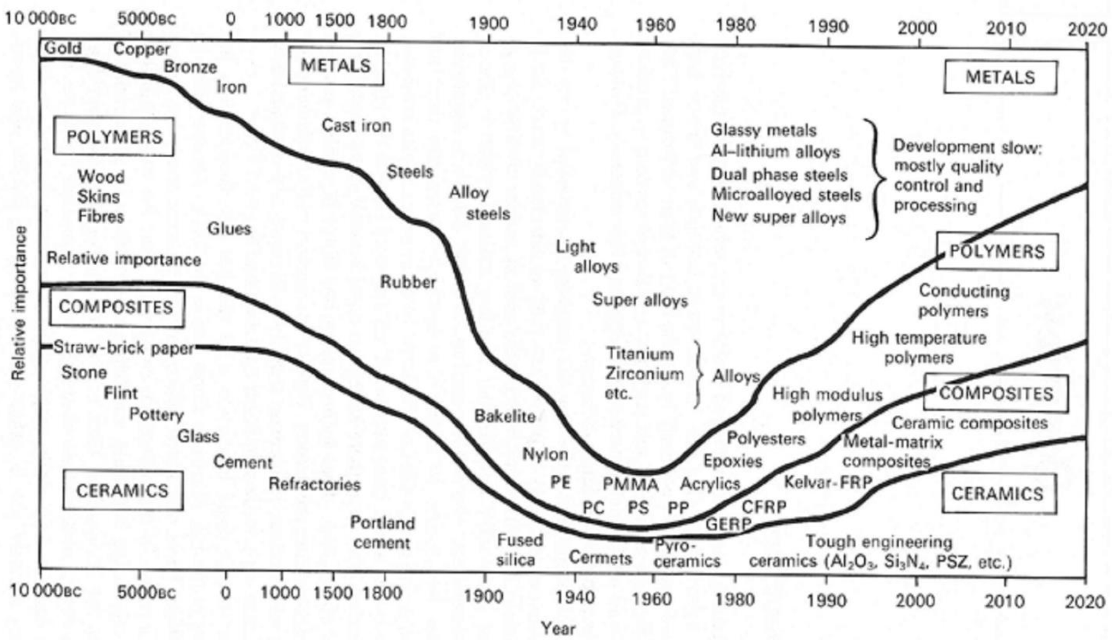


Figure 10. Evolution of engineering materials.

### 1.4.2. Properties of composite materials

In general, composite materials are very anisotropic materials, mainly due to the lack of homogeneity in the distribution and orientation of the reinforcing elements within the matrix.

In other words, the main property that composite materials have is anisotropy, a general property of matter according to which qualities such as elasticity, temperature, conductivity and speed of light propagation vary according to the direction in which they are examined.

On the other hand, strength in composite materials depends on the nature of the reinforcement, their arrangement and orientation in the matrix, and the effectiveness of the reinforcement/matrix interface.

The main advantages of composite materials are the following:

- Excellent mechanical properties.
- High resistance/weight ratio.
- Possibility of building more or less complex shapes.
- Ease of manufacture with a high variety of finishes.
- High resistance to fatigue.
- High rigidity.
- High resistance to corrosion.
- Improved aerodynamic surfaces.
- High dielectric strength.
- Dimensional stability.
- High flexibility.

However, despite all its advantages there are a number of drawbacks [9] such as:

- The high cost of the raw material of these materials. For example, if we compare its price to that of aluminium and steel is very high.
- Lack of information about the final mechanical behaviour that the part made of the composite material will have.
- Sometimes, there are health hazards in the manufacturing processes of some composite materials.
- In the design stage of parts manufactured from composite materials, the existing calculation tools are not as well-known as they are for the design of metal parts.
- Composite materials have the disadvantage that they absorb moisture, affecting their properties and dimensional stability.

## 1.5. Classification of composite materials

As mentioned above, there is a wide range of composite materials. The particular characteristics of each will depend on the type of matrix and reinforcement used.

The different types of matrixes and reinforcements available will be explained below.

### 1.5.1. Matrix

According to the type of matrix we found: Metal matrix composite materials, Ceramic matrix composites and Organic/polymer matrix.

The metal matrix is characterized by a higher capacity to resist the composite material, as well as a good rigidity and tenacity to fracture. Also, it presents a low anisotropy and a good behaviour at high temperatures. There are three types of metal matrix: aluminium alloys, titanium and copper.

However, this type of matrix is limited by its high density, in addition to offering some difficulty for processing.

On the other hand, the ceramic matrix gives the composite part a high resistance to mechanical stress, even at high temperatures without modifying their resistance capacity but its toughness is very low, as are its thermal and electrical conductivities and they are not tensile. For this reason, fibres with high tensile strength are usually added to them.

There are three types of ceramic matrices: alumina, silicon carbide and silicon nitride.

Since this project is based on the use of polymer resins, we will focus especially on explaining the different types of polymer matrix.

The organic or polymeric matrix is characterized by its low density, high toughness, high corrosion resistance, low mechanical resistance, low cost, speed and simplicity of forming.

During the handling of this type of matrix it is necessary to study the influence that environmental conditions can have on the polymers such as temperature, solar radiation and humidity [6].

There are different types of polymeric matrices:

- THERMOPLASTICS, used in low requirement applications, although advanced thermoplastics are starting to be used for high performance.

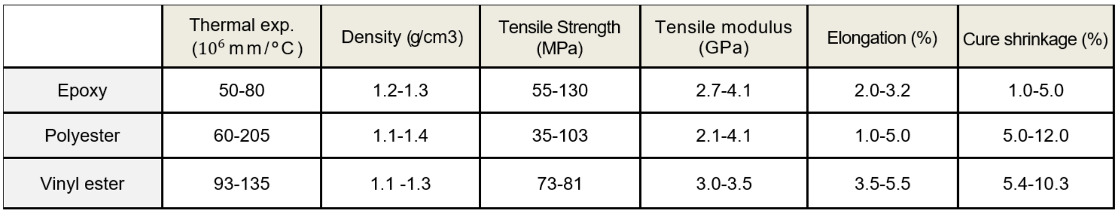
This type of matrix is formed by molecules joined by weak forces, which gives them the property of softening and being able to be shaped by the action of heat, hardening when cooling, so that it would be a reversible process. Some examples are polypropylene, polyethylene and polyamide.

- THERMOSTABLES, the most used in high performance composite materials.

Thermoset organic matrices are characterized by being formed by reticulated chains that make the structure acquire a permanent disposition, causing the reaction to be irreversible. In this type of organic matrix, a curing process is needed to achieve its reticulated structure.

In this project we will focus in more detail on thermoset matrices. Within the group of organic thermoset matrices also called resins, there are different types: unsaturated polyester, epoxy resins, vinyl ester resins and polyurethane resins.

But the most used resins are epoxy resin, polyester and vinyl ester. Their main characteristics are the follows: [10]



| | Thermal exp. ($10^6$ mm/°C) | Density (g/cm3) | Tensile Strength (MPa) | Tensile modulus (GPa) | Elongation (%) | Cure shrinkage (%) |
|---|---|---|---|---|---|---|
| Epoxy | 50-80 | 1.2-1.3 | 55-130 | 2.7-4.1 | 2.0-3.2 | 1.0-5.0 |
| Polyester | 60-205 | 1.1-1.4 | 35-103 | 2.1-4.1 | 1.0-5.0 | 5.0-12.0 |
| Vinyl ester | 93-135 | 1.1 -1.3 | 73-81 | 3.0-3.5 | 3.5-5.5 | 5.4-10.3 |

*Table 1. Characteristics of the main polymer resins.*

### *1.5.1.1. Unsaturated polyester*

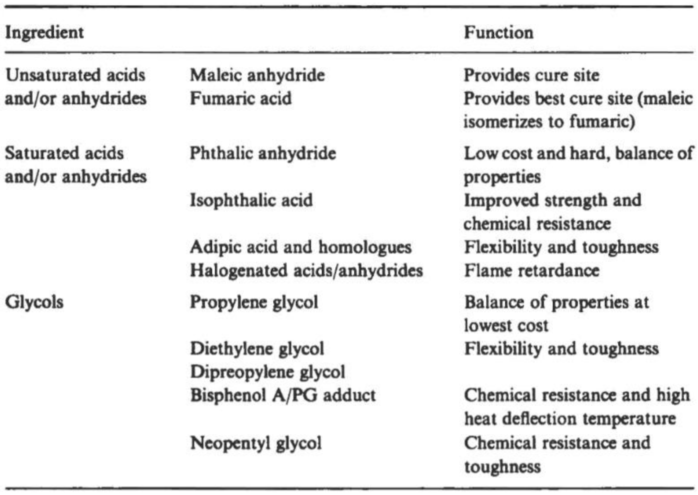
The main characteristics of unsaturated polyesters are that they have good resistance to softening and deformation at high temperature, their electrical properties, resistance to corrosion and to weak alkalis and strong acids, and they have good resistance to weathering.

The unsaturated polyester resins are not the ones that show the best result as a matrix but even so they are widely used in composite applications[11]. The most important applications are in construction, such as building facades, storage tanks and baths and showers, in transport for car body repair and in the shipbuilding industry[12].

Moreover, they are widely used in gel coatings that are used as colour and surface protection coatings in composites. In addition, unsaturated polyester resins are very versatile, as processing into a composite product can be done by various techniques. Hence their use in marine, automotive, electrical and electronic, construction, sport and leisure, household and sanitary appliances, furniture and military applications [13].

The main group that shows this type of resin is the ester group as a linear chain combined with aliphatic groups which do not contain aromatic groups but provide the necessary gaps so that they can react with other unsaturated monomers. The reactions in this type of resin are usually fast but under control to achieve the desired crosslink structure.

The reaction that takes place is a mixture of unsaturated and saturated dicarboxylic acids that react with diols in a polycondensation fusion. Some of the ingredients which can be used to make the unsaturated polyester are in Figure 11. Alcohols and monofunctional acids are also used in some formulations to adapt properties [14].



| Ingredient | | Function |
|---|---|---|
| Unsaturated acids and/or anhydrides | Maleic anhydride | Provides cure site |
| | Fumaric acid | Provides best cure site (maleic isomerizes to fumaric) |
| Saturated acids and/or anhydrides | Phthalic anhydride | Low cost and hard, balance of properties |
| | Isophthalic acid | Improved strength and chemical resistance |
| | Adipic acid and homologues | Flexibility and toughness |
| | Halogenated acids/anhydrides | Flame retardance |
| Glycols | Propylene glycol | Balance of properties at lowest cost |
| | Diethylene glycol | Flexibility and toughness |
| | Dipreopylene glycol | |
| | Bisphenol A/PG adduct | Chemical resistance and high heat deflection temperature |
| | Neopentyl glycol | Chemical resistance and toughness |

*Figure 11. Some ingredients of unsaturated polyesters.*

Thanks to the possibility of making variations in the basic components of the polyester chain and the radius of saturated and unsaturated components, a wide range of resins can be obtained according to specific requirements.

Unsaturated polyester has a molecular mass between 1000 and 5000. The molecular mass is regulated by the diol/dicarboxylic acid ratio, according to Carothers' principles.

Thus, by adjusting the molar ratio of unsaturated dicarboxylic acid and saturated dicarboxylic acid, the desired properties of the resin can be obtained. For example, the reactivity of the unsaturated polyester and the crosslink density of the final net can be controlled.

In this manner, if the saturated dicarboxylic acid is used in a molar excess, the reactive unsaturated bonds will be distributed in the polyester chain in a dispersed way, and the reactivity of the unsaturated polyester will be lower.

On the other hand, if unsaturated dicarboxylic acid is used in a molar excess, the reactive double bonds will be distributed with greater density, and the reactivity will be higher, since there will be a greater number of reactive sites on each polyester chain. In this case the final resin will be more brittle and therefore worse mechanical properties.

For this reason, commercial unsaturated polyesters are usually formulated using an excess of saturated acid.

Due to their low cost, about 80% of unsaturated polyester resins are orthophtalic resins where orthophtalic acid is used as the saturated acid part of the polymer structure.

#### *1.5.1.2. Epoxies*

Epoxy resins are used in many applications, such as surface coatings, printed circuit boards, electronic component packaging, rigid foams, adhesives and fibre-reinforced compounds.

This requires a curing process where the monomeric or oligomeric polyfunctional epoxy is transformed into a cross-linked macromolecular structure.

The curing reactions of epoxy resins involve the opening of the epoxy ring, followed by a homopolymerization reaction with more epoxides or a reaction with other species to form addition products.

This curing process together with the available control and monitoring techniques can result in a final product with the desired properties [15].

However, there are some difficulties during curing reactions. For example, the isothermal curing reaction of an epoxy resin is often complicated as large changes occur in the macroscopic physical properties of the reaction system due to the interaction of the chemical curing kinetics with other physical processes such as gelling, phase separation, vitrification and devitrification [16,17].

For this reason, it is of great importance to study the kinetics of curing reactions by means of techniques such as Fourier transform IR, infrared spectroscopy, direct current conductivity or thermal analysis such as differential scanning calorimetry (DSC). The technique that has published the best results and reviews to study the curing reaction has been the application of DSC.

The differential scanning calorimetry technique is used to monitor the curing reaction and to evaluate the thermal properties of the resin during curing.

Approximately 75% of the epoxy resins currently used worldwide are derived from liquid epoxy resins (Diglycidyl ether of bisphenol A, DGEBA) (Figure 12) [18].

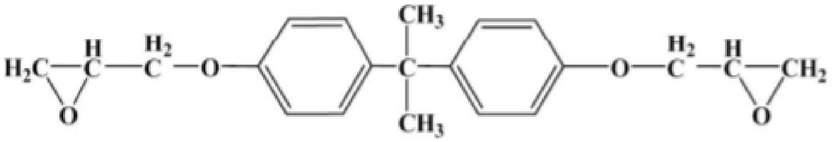


*Figure 12. Structure of a typical epoxy (diglycidyl ether of bisphenol-A) resins.*

This market dominance of bisphenol A-based epoxy resins is the result of a combination of their relatively low cost and high performance in different applications such as tools, castings, adhesives, coatings and composites.

In fact, epoxy resins are being highly demanded in Europe in the wind sector for the construction of new wind farms because their use in the manufacture of windmill blades allows them to be made longer as well as providing better resistance and fatigue properties.

#### *1.5.1.3. Vinyl esters*

Vinyl ester resin is produced from the esterification of an epoxy resin with methacrylic or acrylic acids.

Both the majority of properties and the cost of vinyl esters are intermediate between epoxy resins and unsaturated polyesters. Vinyl ester resins fall between polyester and epoxy in terms of price, and in most of their physical properties and handling qualities. However, vinyl ester resins exceed both polyester and epoxy in corrosion resistance, temperature resistance, and toughness.

That is, vinyl ester resins are quite similar to unsaturated polyester resins as both have a low viscosity and low cure time. But they differ in that they are a few times more expensive than unsaturated polyesters but less than high performance epoxy resins.

They also have high chemical and mechanical performance. These types of resins are normally used because they are easy and fast to process and because of their good resistance to wet environments [7].

They are especially applied in high performance gel coatings, reaction tanks and pipelines. Also, they also applied in the construction of windmill blades in the wind energy industry [18].

Vinyl-ester resins were developed especially for applications in corrosive environments, such as pipe linings and tanks filled with hazardous chemicals.

#### *1.5.1.4. Polyurethane resins*

Polyurethane resins are copolymers composed of isocyanate and polyol components. Polyols contain -OH groups and an isocyanate containing an NCO group.

The polyurethanes can be synthesized in a single step by directly mixing the components or by the prepolymer method. The latter involves the addition of diol and isocyanate to form the polyurethane prepolymer with NCO as the final groups. This prepolymer is then grown with chain extenders to form the polyurethanes [19].

Its main characteristics are its high adhesion to the substrates, an excellent balance of hardness and elongation and a high elasticity of the film. For this reason, they are used in applications such as the treatment of metals, coatings, adhesives, highlighting their use as electrical insulation materials, providing significant protection of electrical equipment against aggressive media such as water, chemicals and dust [20].

Polyurethane resin is considered versatile because it can be used to produce a variety of items, from inks to plastics, as this material can be manipulated to great extremes and therefore change its properties from, for example, a flexible and soft rubber to a very hard and rigid plastic.

Considering them hard, the clear advantage over other types of dies is reflected in their great hardness and elasticity. In comparison with other thermosetting resins, polyurethane resins can work as fast as polyesters, but they perform mechanically and thermally in the vicinity of epoxies.

Polyurethane resins also have the great advantage that they are resistant to chemicals, oils and greases and to abrasion.

### 1.5.2. Reinforcement

As for the reinforcements we find different types, such as: carbon fibres, glass fibres, aramid fibres and natural fibres since it is possible to obtain materials with discontinuous reinforcements (particles, platelets or short fibres) or materials with continuous reinforcements (long fibres, fabrics or laminates)[21].

The reinforcement phase of a composite material can be found in different forms: in the form of fibres, particles of different shapes and in the form of whiskers. Depending on the type of shape, the different hardness and rigidity of the final composite material is achieved [22].

In the form of particles, it may be spherical, cubic, tetragonal, platelet, or otherwise regular or irregular, but it is roughly equiaxid. When it is a fibre type, it is characterised in that its length is much greater than its transverse dimensions.

Therefore, the properties that are achieved by fibres depend especially on the way the fibres are placed in the composites. That is, for each composite material one type of form or another will be used. The important thing to remember about composites is that the fibre carries the load and its strength is greater along the fibre axis.

When the reinforcement is in the form of a fibre, it can be classified into two groups: continuous or long fibres and discontinuous or short fibres (Figure 13).

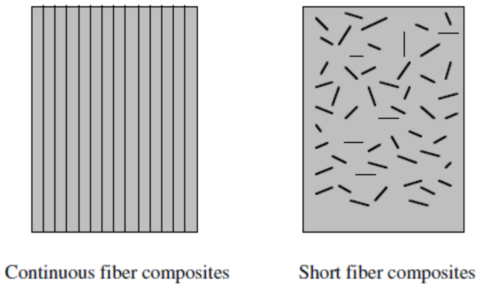
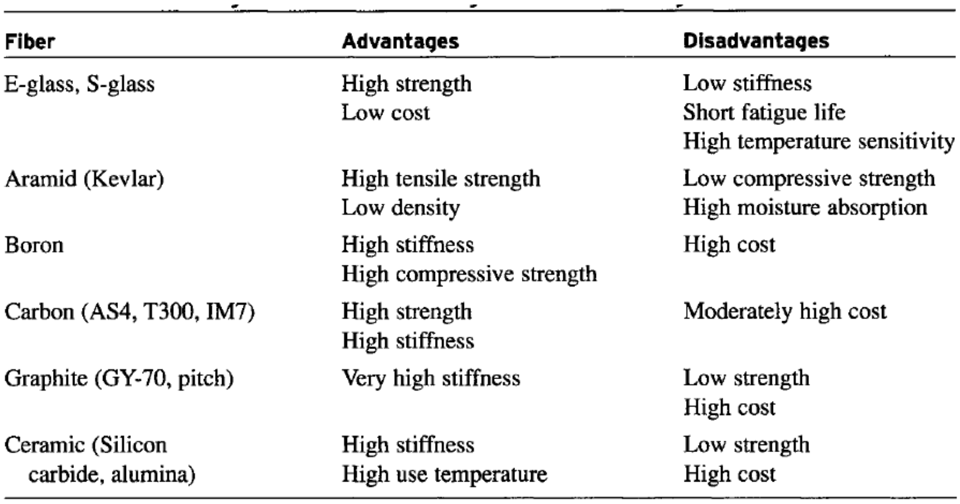


*Figure 13. Continuous and short fibre composites.*

One of the differences between both is that in a discontinuous fibre composite the fibre length affects the properties of the composite and in continuous fibre reinforced composites the load is applied directly to the fibres so that the fibres in the direction of the load are the main load-carrying component. The latter assumption is particularly valid when high modulus fibres are used in large concentrations [23].

Long continuous fibres in the direction of loading result in a composite material with properties that exceed the matrix resin itself. The same material cut into short lengths produces properties that are inferior to those of continuous fibres. This is why the choice of fibre shape is so important depending on the type of application (structural or non-structural). Long or continuous fibres are recommended for structural applications and short fibres for non-structural applications [24].

Therefore, there is a wide variety of fibres available. In the Figure 14 below we can see the different advantages and disadvantages corresponding to the different types of fibres as reinforcements. Generally, the desirable characteristics of most reinforcement fibres are high strength, high stiffness and relatively low density.



| **Fiber** | **Advantages** | **Disadvantages** |
|---|---|---|
| E-glass, S-glass | High strength<br>Low cost | Low stiffness<br>Short fatigue life<br>High temperature sensitivity |
| Aramid (Kevlar) | High tensile strength<br>Low density | Low compressive strength<br>High moisture absorption |
| Boron | High stiffness<br>High compressive strength | High cost |
| Carbon (AS4, T300, IM7) | High strength<br>High stiffness | Moderately high cost |
| Graphite (GY-70, pitch) | Very high stiffness | Low strength<br>High cost |
| Ceramic (Silicon carbide, alumina) | High stiffness<br>High use temperature | Low strength<br>High cost |

*Figure 14. Advantages and Disadvantages of Reinforcing fibres.*

For this reason, when choosing it, special interest is generally taken in the stress vs. tensile strain curves of the different types of reinforcing fibres, in addition to the behaviour of their specific strength vs. specific modulus (Figure 15).

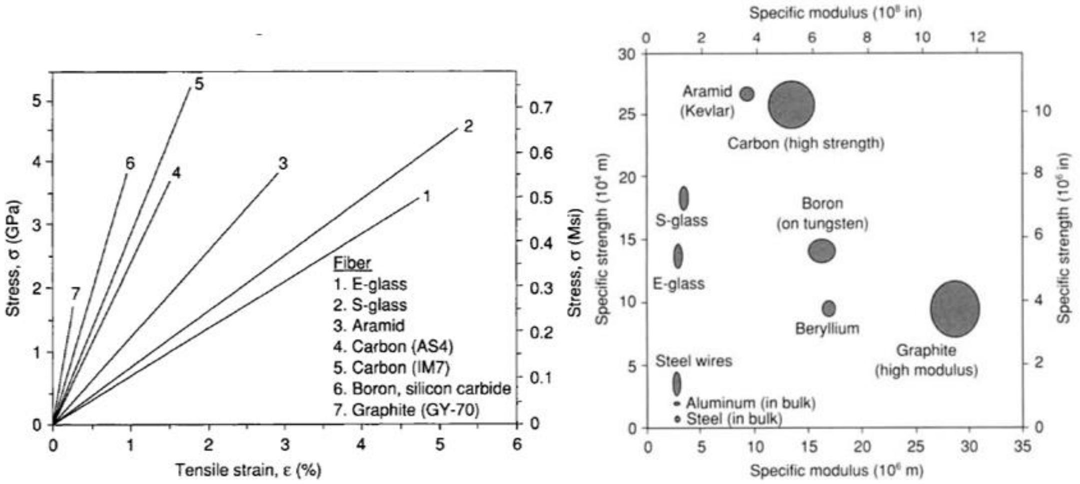


*Figure 15. Representation of the Stress vs Tensile Strain and the Specific Strength vs Specific Modulus of typical reinforcing fibres.*

In the case of the fibres, flexibility is a very important factor to take into account as it determines whether the fibres can be easily woven or not and therefore influences the choice of the manufacturing method of the composite material [25].

The flexibility of a fibre depends mainly on Young's modulus Ef, and the diameter D of the fibre as we can see in the following equation:

$$\text{Flexibility},\ \alpha \frac{1}{E_t D^4}$$

Thus, large diameter fibres with a high Young's modulus will not be flexible.

The mechanical properties of the fibres of a given type and dimensions are also determined by the structure. For example, the properties of the organic fibre, aramid, depend on the orientation of the molecular structure, while for carbon fibres the perfection and alignment of the graphite crystals are paramount as we will see in more detail below.

At present, many materials are being replaced, mainly metallic ones, by one of the most commonly used composite materials such as polymeric matrix materials with reinforcements in the form of fibres. These, thanks to their lightness and excellent mechanical properties, are very successful in those applications where the relationship 'mechanical properties - weight' has a decisive influence on the maintenance costs of the product.

The main fibres used as reinforcements are: glass fibres, carbon fibres, boron fibres, ceramic fibres, metal fibres, aramid fibres and natural fibres. But the most widely used fibre materials in fibre-reinforced polymer (FRP) are glass, carbon and aramid.

#### *1.5.2.1. Glass fibres*

Polyester-glass composites (GFRPs) are the cheapest and by far the most widely used in low to medium performance due to their high tensile strength [22].

Glass fibres are materials made of extremely fine fibreglass which is a non-crystalline material with a short-range network structure. As such it does not have a distinctive microstructure and the mechanical properties that are mainly determined by the composition and finish of the surface are isotropic.

There are many groups of glass, for example, silica, oxynitro, phosphate and halide glasses, but from the point of view of compound technology only silica glasses are important today (Figure 16). The other components are added depending on the desired properties.

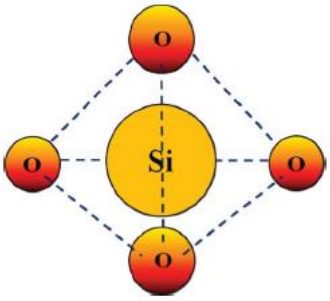


*Figure 16. Molecular structure of silica glass fibre.*

The types of glass fibres most commonly used are mainly E-glass used generally for glass reinforced polymers, A-glass, E-CR-glass, C-glass which offers chemical stability, D-glass used for example in applications where a low dielectric constant is required, R-glass and S-glass used when greater resistance and rigidity is required among others. The compositions of some typical glass fibres which are used in the manufacture are given in the following Figure 17:

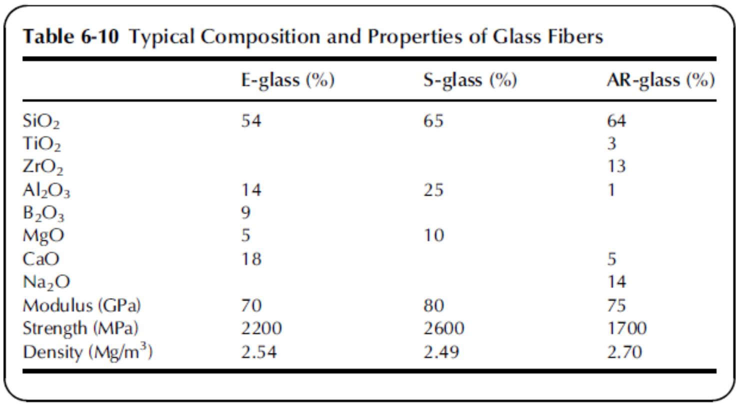


**Table 6-10** Typical Composition and Properties of Glass Fibers

| | E-glass (%) | S-glass (%) | AR-glass (%) |
|---|---|---|---|
| $SiO_2$ | 54 | 65 | 64 |
| $TiO_2$ | | | 3 |
| $ZrO_2$ | | | 13 |
| $Al_2O_3$ | 14 | 25 | 1 |
| $B_2O_3$ | 9 | | |
| MgO | 5 | 10 | |
| CaO | 18 | | 5 |
| $Na_2O$ | | | 14 |
| Modulus (GPa) | 70 | 80 | 75 |
| Strength (MPa) | 2200 | 2600 | 1700 |
| Density ($Mg/m^3$) | 2.54 | 2.49 | 2.70 |

*Figure 17. Typical properties and composition of Glass Fibres.*

The process of manufacturing glass fibres involves first mixing the raw materials and melting them in a furnace. The resulting melt then flows through one or more bushings containing hundreds of small holes. In this way, glass filaments are formed as the molten glass passes through these holes. Finally, the formed glass filaments are rapidly cooled below the transition temperature of the glass by water and/or air [9].

#### *1.5.2.2. Carbon fibres*

Carbon fibres are the most commonly used for advanced composites.

Depending on the manufacturing process they have different degrees of strength and stiffness. In particular, this type of fibre is anisotropic both mechanically and thermally due to in the radial direction the stiffness is much lower and the coefficient of thermal expansion much higher than in the axial direction.

There are two manufacturing routes: either from organic precursor fibres by pyrolysis, such as rayon or polyacrylonitrile (PAN), or from petroleum pitch.

In both cases, the precursors are first oxidized at extremely high temperatures. Then, they go through carbonization processes where the precursors undergo chemical changes resulting in properties such as high rigidity and weight resistance.

PAN refers to polyacrylonitrile, a polymer fibre of textile origin. Pitch fibre is obtained by spinning purified petroleum or coal tar pitch. PAN-based fibres are most widely used for the fabrication of carbon fibres. Pitch-based fibres tend to be stiffer and more brittle.

Carbon fibres are made up of fine carbon filaments of 5-10 µm in diameter, where each carbon fibre is formed by the union of thousands of carbon filaments (Figure 18).

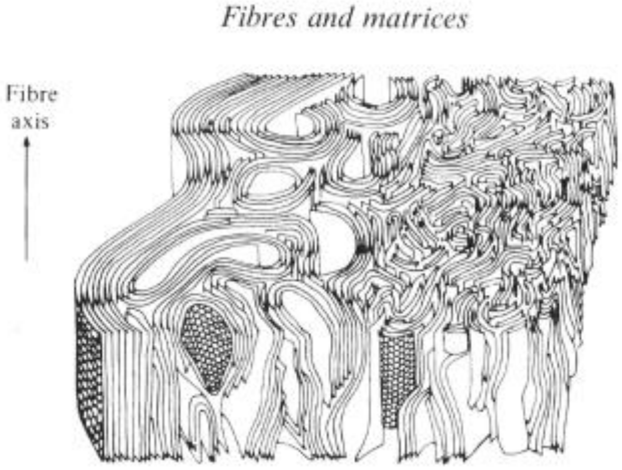


Figure 18. Structure of carbon fibres.

Carbon fibre is an electrically conductive material with high thermal conductivity and has the characteristic of high strength and rigidity as well as high hardness.

Carbon atoms are bound together in microscopic crystals that are more or less aligned parallel to the long axis of the fibre. The alignment of the crystals makes the fibre very strong for its size [25].

Its excellent mechanical properties, together with its low density, generates great applications in the aerospace industry, civil engineering, military and motor sports. Especially, for low-weight applications due to its density is lower than that of steel, making it ideal.

There are different types of carbon fibre in terms of their mechanical resistance with respect to their modulus of elasticity: high modulus, high strength, ultra-high modulus, and ultra-high strength.

Carbon fibre reinforced polymer (CFRP) composites offer greater stiffness and strength than Glass fibre reinforced polymer, but they are considerably more expensive. Also, they are very strong when stretched or bent, but weak when compressed or exposed to strong shocks.

#### *1.5.2.3. Aramid fibres*

Aramid fibres are processed in such a way that polymer chains line up parallel to the fibre axis. Aramid fibres are produced by extrusion of an acid solution (a patented polycondensation product of terephthalloyol chloride and p-phenylenediamine) through a row [9]. That is, it is the union of an aromatic polyamide with a ring structure that produces a high rigidity; the covalent union of the chain produces high resistance.

The most well-known aramids (Nomex, Kevlar, Twaron, X-fiper, and New Star) are AABB polymers [25].

Kevlar was originally produced by Dupont. There are different types: low density/high strength cables (Kevlar 29) generally used in cables, ropes and body frames, high modulus (Kevlar 49) in aerospace, maritime and automotive applications and ultra-high module applications (Kevlar 149) [24].

Kevlar fibres have greater stiffness than glass fibres and their density is approximately half that of glass fibres. They also have high tensile strength, and excellent hardness and impact resistance. Due to their high molecular orientation they are very anisotropic mechanically and thermally [22]. However, Kevlar compounds have very low resistance to longitudinal compression and transverse tension and are sensitive to moisture absorption.

On the other hand, Nomex fibres have excellent flame and abrasion resistance. They are generally used for the manufacture of structural honeycombs. These materials are exceptionally stable and have good strength, hardness, and rigidity up to a temperature of 170ºC.

In general, aramid fibres provide the highest tensile-weight ratio between reinforcing fibres. They also provide good impact resistance. However, their main disadvantage is that they are difficult to cut and machine.

#### *1.5.2.4. Natural fibres*

Natural fibres play a very important role today as reinforcement for composite materials as they are considered to be ecological materials with good properties.

By definition, natural fibres are those that come from plants and animals and therefore are not synthesized or manufactured by man.[26]

Today, the most important renewable and non-renewable natural fibres used in the manufacture of composite materials are those from oil palms, sisal, flax and jute.

Generally, plants from which natural fibres are obtained can be classified as bast fibres (jute, flax, ramie, hemp and kenaf), seed fibres (cotton, coir and kapok), leaf fibres (sisal, pineapple and abaca), grass and cane fibres (rice, maize and wheat) and core fibres (hemp, kenaf and jute), as well as all other types (wood and roots) [27].

Figure 19 shows the production of the most common and commercial natural fibres worldwide.

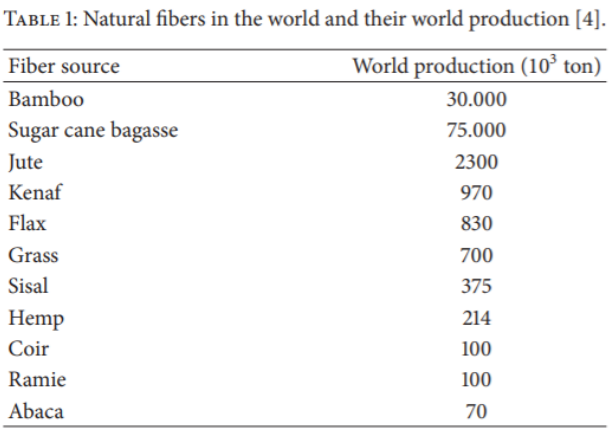


Table 1: Natural fibers in the world and their world production [4].

| Fiber source | World production ($10^3$ ton) |
|---|---|
| Bamboo | 30.000 |
| Sugar cane bagasse | 75.000 |
| Jute | 2300 |
| Kenaf | 970 |
| Flax | 830 |
| Grass | 700 |
| Sisal | 375 |
| Hemp | 214 |
| Coir | 100 |
| Ramie | 100 |
| Abaca | 70 |

*Figure 19. World production of natural fibres.*

Compared to synthetic fibres, natural fibres are superior in terms of relatively low weight, low cost, less damage to processing equipment, good relative mechanical properties such as tensile and flexural modulus, better surface finish of composite castings, renewable resources, abundance, flexibility during processing, biodegradability and minimal health risks. [28]

Despite the many advantages, natural fibres have significant deficits in their properties. For example, they tend to absorb moisture causing a weak bond between the fibre and the polymer.

Applications of natural fibres are growing rapidly in many fields of engineering. Some of these are the automotive, construction, aerospace and sports industries.

## 1.6. Composites processing

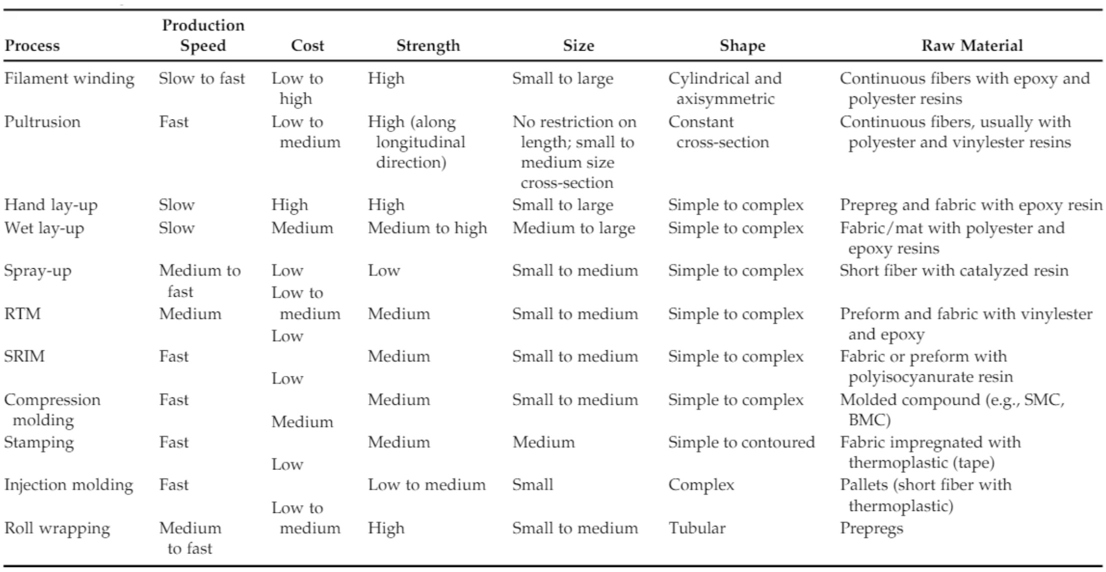
Since obtaining composite materials involves two or more different materials, the use of processing techniques is necessary.

Nowadays, we have different processing techniques to obtain the composite materials where the different types of matrixes and reinforcements are worked.

The processing technique chosen to carry out the manufacture of a particular composite material will be selected to meet the specific requirements of performance, cost and rate of production.

Therefore, this choice is a great challenge for the engineer who must carry it out taking into account the selection criteria such as cost, strength, production rate, and especially the requirements of the shape and size of the final part.

The Figure 20 shows the different types of processes according to the selection criteria mentioned above.



| Process | Production Speed | Cost | Strength | Size | Shape | Raw Material |
|---|---|---|---|---|---|---|
| Filament winding | Slow to fast | Low to high | High | Small to large | Cylindrical and axisymmetric | Continuous fibers with epoxy and polyester resins |
| Pultrusion | Fast | Low to medium | High (along longitudinal direction) | No restriction on length; small to medium size cross-section | Constant cross-section | Continuous fibers, usually with polyester and vinylester resins |
| Hand lay-up | Slow | High | High | Small to large | Simple to complex | Prepreg and fabric with epoxy resin |
| Wet lay-up | Slow | Medium | Medium to high | Medium to large | Simple to complex | Fabric/mat with polyester and epoxy resins |
| Spray-up | Medium to fast | Low | Low | Small to medium | Simple to complex | Short fiber with catalyzed resin |
| RTM | Medium | Low to medium | Medium | Small to medium | Simple to complex | Preform and fabric with vinylester and epoxy |
| SRIM | Fast | Low | Medium | Small to medium | Simple to complex | Fabric or preform with polyisocyanurate resin |
| Compression molding | Fast | Low | Medium | Small to medium | Simple to complex | Molded compound (e.g., SMC, BMC) |
| Stamping | Fast | Medium | Medium | Medium | Simple to contoured | Fabric impregnated with thermoplastic (tape) |
| Injection molding | Fast | Low | Low to medium | Small | Complex | Pallets (short fiber with thermoplastic) |
| Roll wrapping | Medium to fast | Low to medium | High | Small to medium | Tubular | Prepregs |

*Figure 20. Manufacturing process selection criteria.*

However, each manufacturing method uses a specific type of raw material for the manufacture of parts. That is, what for a raw material there is a suitable manufacturing method, may not be so for another type of manufacturing system. [9]

For example, if our raw material is in granulated form, we know that we can use the injection moulding manufacturing method and we cannot use the pultrusion method.

Any manufacturing process of the specific composite material requires four steps that depending on the type of composite material are performed in one way or another.

The four general primary steps are: wetting/impregnation, lay-up, consolidation and solidification.

- Impregnation

In this step, a sheet is formed by mixing the fibres and the resins. So, the purpose of this stage is that the resin is completely around the fibres.

For example, in a winding process of filaments, the fibres are taken to a resin bath where they are impregnated.

If we are dealing with a manual lamination process, pre-pregs are used that have already been impregnated by the supplier of the material. On the other hand, in a wet lamination process, by using a compression roller, each layer of fabric is impregnated with resin by wetting it.

Viscosity, surface tension and capillary action are the main parameters affecting the impregnation process.

- Lay-up

The aim of this step is to achieve the fibre structure according to the design, since the structure of the composite material depends largely on the orientation and design sequence of the fibre that composes it.

To achieve this, composite laminates are formed by placing the mixture of resins or pre-impregnated fibres at the desired angle and location. To obtain the desired thickness, several layers of the resin-fibre mixture are placed.

- Consolidation

The purpose of this step is to ensure that all air that may have been trapped between the layers is removed during the processing step so that intimate contact between the layers is created. In short, this stage is very important to obtain a high-quality final result.

- Solidification

Finally, in the last step the time necessary to carry it out differs greatly depending on the type of composite material.

For example, in thermosetting composites, the solidification rate depends on the resin formulation and the cure kinetics. In this case heat is supplied during processing to speed up the cure rate of the resin.

In other cases, such as thermoplastic composites, there is no chemical change during solidification and therefore solidification requires the least amount of time.

In the following Figure 21 we can see the different processing techniques of the composite materials according to the state of their material. Generally, these are divided into two groups, the thermoplastic-based composite materials which are those that can be reformed once they have solidified and the thermostable-based ones, which once they have reached their cured state and therefore solidified cannot be melted again.

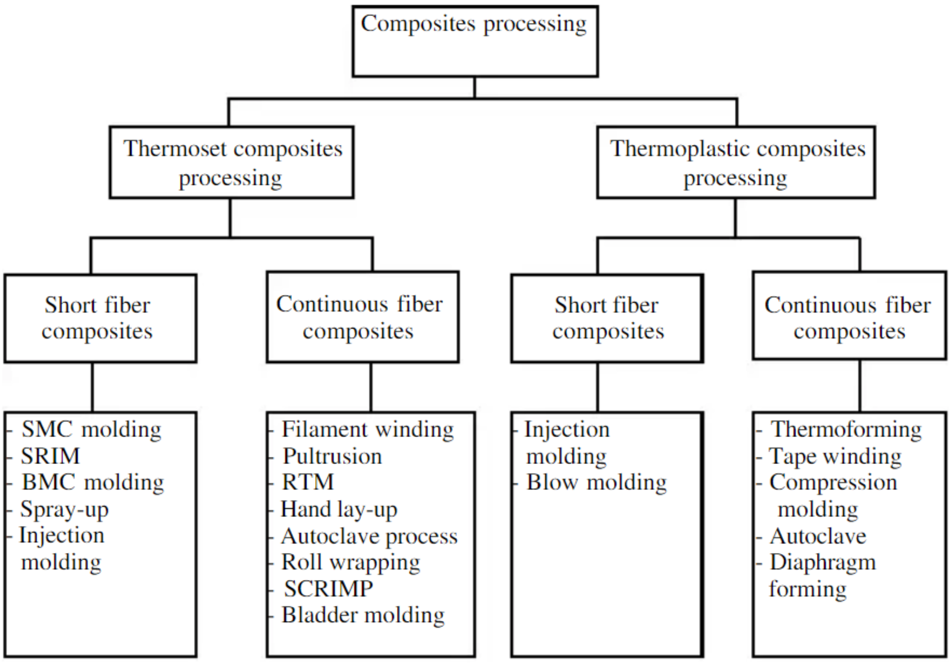


*Figure 21. Classification of composites processing techniques.*

### 1.6.1. Thermosetting composite manufacturing

Between the two groups, thermosetting composite materials dominate the market. About 75% of all composite products are made from thermosetting resins. Hence, existing processes for thermosetting composites are more advanced and have better advantages over processing thermoplastic composite materials.

We will therefore focus in more detail on processing techniques for thermoset composite materials. The different types of processing that exist are: Lay-up process, filament winding process, pultrusion process, resin transfer moulding process, structural reaction injection moulding (SRIM) process, compression moulding process, roll wrapping process and finally injection moulding of thermoset composites.

#### *1.6.1.1. Lay-up process*

Lay-up processes are ideally suited for the manufacture of low-volume medium-to-large parts. These processes are capable of making very large parts with minimal tooling costs, such as custom-built yacht hulls.

However, manual lay-up processes are labour intensive and therefore the final result of the parts will depend largely on the skill and qualities of the worker.

Within this group, three types of manual lay-up processes stand out: wet lay-up, spray-up and low-temperature curing/vacuum bag (LTVB) prepreg lay-up.[29]

The first technique wet lay-up process is mainly used for the manufacture of composite parts. It is largely used in the marine industry as well as for the manufacture of prototype parts.

This process, as shown in Figure 22, consists of first applying the liquid resin to the mould and then placing a reinforcement on top. A roller is used to impregnate the fibre with the resin. Another layer of resin and reinforcement is applied until a suitable thickness is built up. [30]

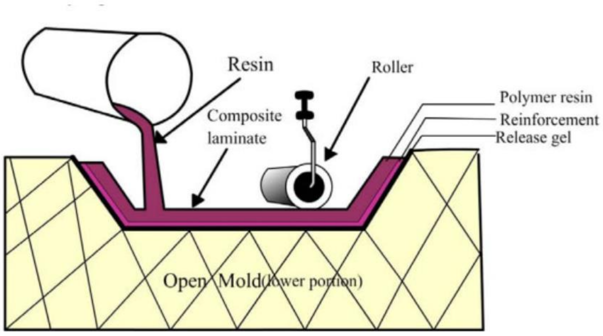


Figure 22. Wet lay-up or hand lay-up process.

This is a very flexible process that allows the user to optimize the piece by placing different types of fabric and carpet materials. This process requires little capital investment.

On the other hand, we have the spray-up process which is a similar method to wet lay-up process. However, greater shape complexity is possible with spray-up.

In the spray-up process (Figure 23), a spray gun is used to apply the resin and reinforcements. In this way, the spray gun deposits the chopped glass fibre and resin/catalyst into the mould and simultaneously cuts continuous fibs into a predetermined length and propels them through a resin/catalyst spray onto the mould.

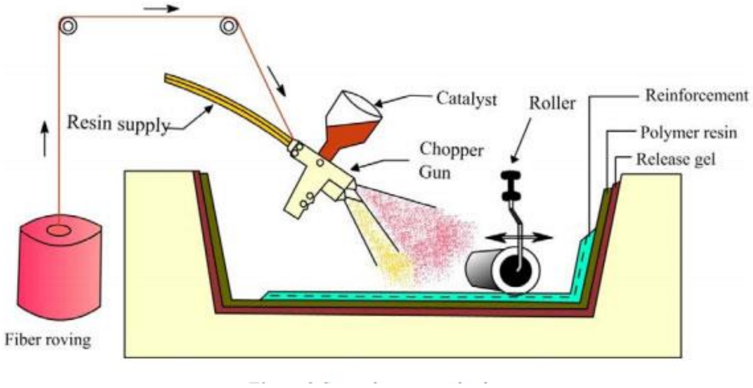


Figure 23. Spray-up process.

As with the wet lay-up process, the major advantages are low cost tooling, simple processing, portable equipment that permits on-site fabrication and virtually unlimited part sizes.

This process compared to the wet lay-up process is much faster and less expensive because it uses rovings, which is a cheap form of fibreglass. An additional advantage of spray-up is it is very amendable to automation, thereby reducing labour costs and the exposure of workers to potentially hazardous fumes.

Finally, the last technique prepreg lay-up, also called the autoclave processing or vacuum bagging process, is an open moulding process with low-volume capability as wet lay-up and spray-up processes.

In this process, prepregs are cut, laid down in the desired fibre orientation on a tool, and then vacuum bagged. After vacuum bagging, the composite with the mould is put inside an oven or autoclave and then heat and pressure are applied for curing and consolidation of the part (Figure 24).

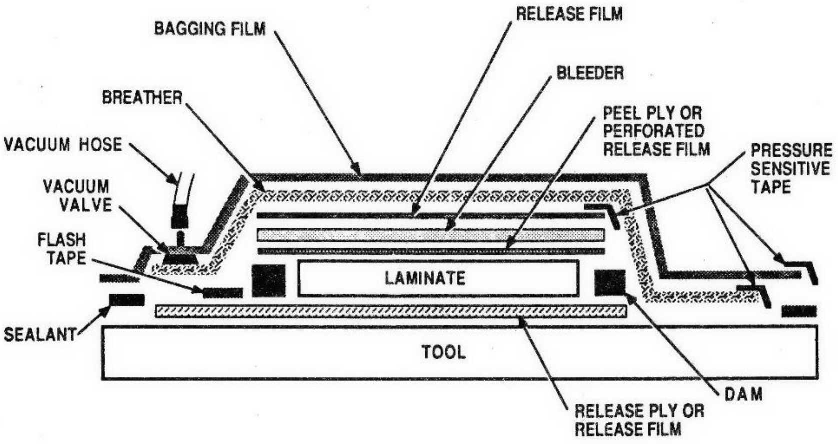


*Figure 24. Prepreg lay-up or vacuum bagging process.*

Complicated shapes with very high fibre volume fractions can be manufactured using this process for this reason, its main application is in the aerospace industry.

The advantages of these method over the rest lay-up techniques are: being a prepreg the resin content is much more tightly controlled; there is no chance for mixing errors that can occur with liquid resins. Also, much higher fibre volumes are obtainable and these materials are net resin content prepregs that do not require bleeding excess resin during cure. Moreover, they are available in both unidirectional tape and woven cloth product forms.

But the main disadvantages are its labour intensive and its cost. The labour costs are 50 to 100 times greater than filament winding, pultrusion, and other high-volume processes. However, its cost is offset by the labour involved in wet lay-up to mix the resin, impregnate the dry plies and then roll out air and excess resin.

### *1.6.1.2. Compression moulding process*

The compression moulding technique is very popular in the automotive industry due to its high-volume capacity as it is used to mould large automotive panels because of its similarity to the stamping process. However, unlike stamping, the final part is manufactured in a single moulding operation. This process is also used to make structural panels using prepregs and basic materials.

Sheet Moulding Compounds (SMC) and Bulk Moulding Compounds (BMC) are the most common raw materials for compression moulding.

In this process (Figure 25), the filler material is placed over the middle of the preheated bottom mould and the filler places are selected for uniform flow across the surface, as well as for better mechanical performance.

The top half of the mould is then quickly closed causing the charge to flow rapidly into the cavity. Finally, after the curing cycle, the top half of the mould moves backwards releasing the pressure from the mould and the final part is demoulded with the help of ejector pins.

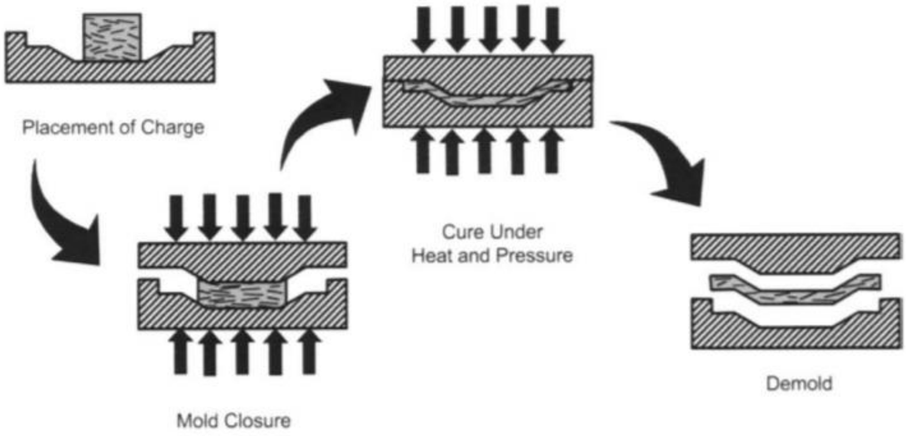


*Figure 25. Compression moulding process.*

It is one of the most economical processes for the manufacture of large series of medium/large sized parts, although the volume of thermosets transformed by this technique has fallen, due to the optimisation of other processes with greater production power.

In the case of using pre-pregs, the process consists of filling the moulding cavity with a pre-peg (mixture of various components) in the form of a sheet and, by means of a combined process of pressure and temperature, obtaining the final part as a result of the curing of the resin. This pre-peg can be moulded directly in a press, without the need to cut it.

The main advantages of this manufacturing process are:

- High volume of production.
- High reproducibility capacity.
- Two good sides.
- Low working requirements.
- Great design flexibility.
- Weight reduction.

### *1.6.1.3. Injection moulding*

Injection moulding is most common in the thermoplastics industry but has also been used successfully in the thermoset industry.

Unlike thermoplastics, processing thermoset compounds by injection moulding requires that both the injection screw or plunger and the moulding machine chamber work at low temperatures. In this way, the mould itself is heated to 250-400 ºF instead of cooling as for thermoplastics. It is important that during the processing stage, there is precise control of the temperature and cycle time to prevent the resin from gelling in the barrel.

In this case, low viscosities of the resin are required for a period of time, but they cure quickly. Particulate fillers, chopped glass fibres and short milled fibres (<0.80 inch) can be used as reinforcement; however, when chopped glass fibres and short milled fibres are used as fillers, the viscosity is higher than with the use of particles and therefore they are more difficult to mould.

This process involves injecting a fixed amount of material into heated mould cavities. After the curing stage, the mould is opened and the part is dropped into a receiving container as we observe in Figure 26.

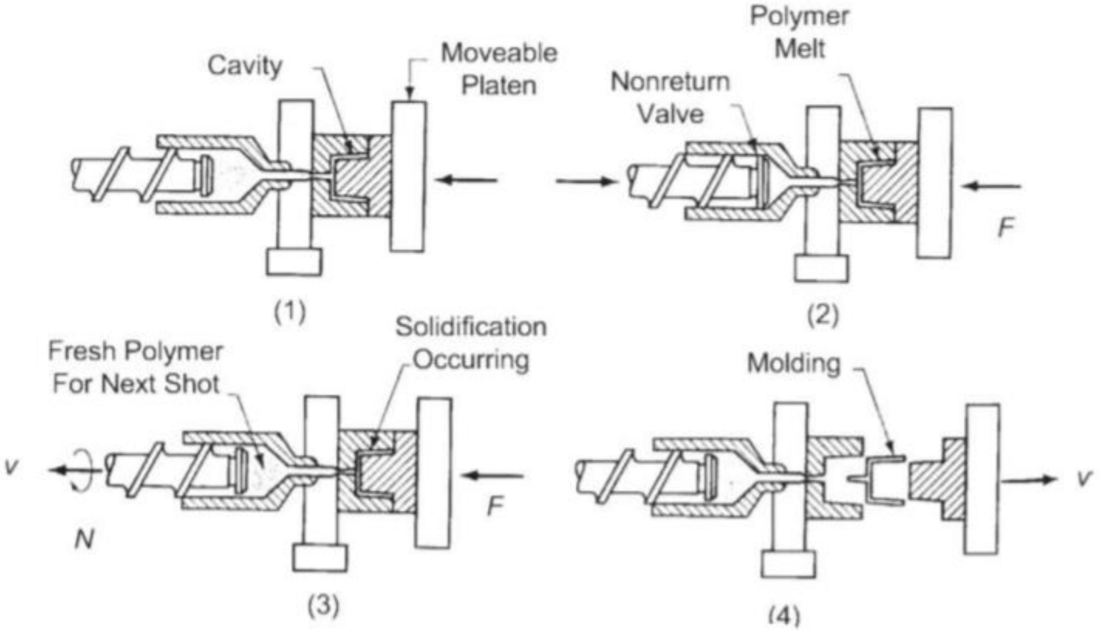


*Figure 26. Injection Moulding Process.*

Injection moulding has the shortest process cycle time compared to any other moulding operation and therefore has the highest production rate. In addition, the production rate can be increased by incorporating a multi-cavity mould.

Due to its high-volume manufacturing it is used in consumer, automotive and recreational applications.

### *1.6.1.4. Reaction injection moulding (RIM)*

Reaction injection moulding (RIM), is used to quickly manufacture unreinforced thermoset parts.

The process involves injecting a highly reactive two-component resin system into a closed mould where the resin reacts and cures rapidly. The resins used must have low viscosities and fast curing cycles in order to be injected at low pressures.

The two components are kept separate and constantly recirculated at high pressure and then mixed in a dynamic mixing head under high pressure and at high speed (Figure 27).

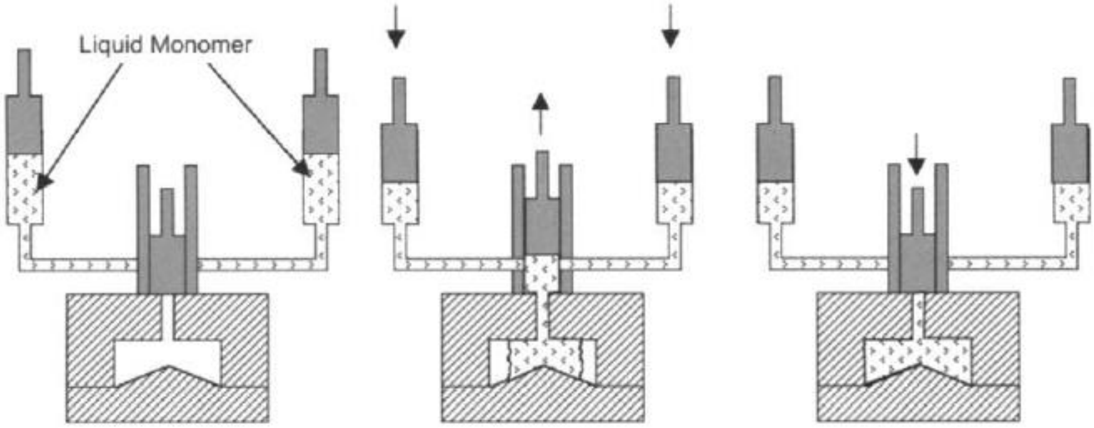


*Figure 27. Reaction injection moulding process (RIM).*

This process in turn is divided into two types of technologies due to the various types of fillers: reinforced reaction injection moulding (RRIM) and structural reaction injection moulding (SRIM).

RRIM is similar to RIM, except that short glass fibres are added to one of the resin components.

Structural reaction injection moulding (SRIM) is similar to RRIM and RIM except that a continuous glass preform is placed in the die prior to injection. The latter technique is similar to the RTM process but in this case, it cannot produce part sizes as large as RTM and also produces parts with higher porosity.

### *1.6.1.5. Pultrusion process*

Pultrusion is a process where the continuous fibre reinforcement is impregnated with a matrix and then is continuously consolidated into a solid composite. [31]

A general scheme of the pultrusion process is shown in Figure 28.

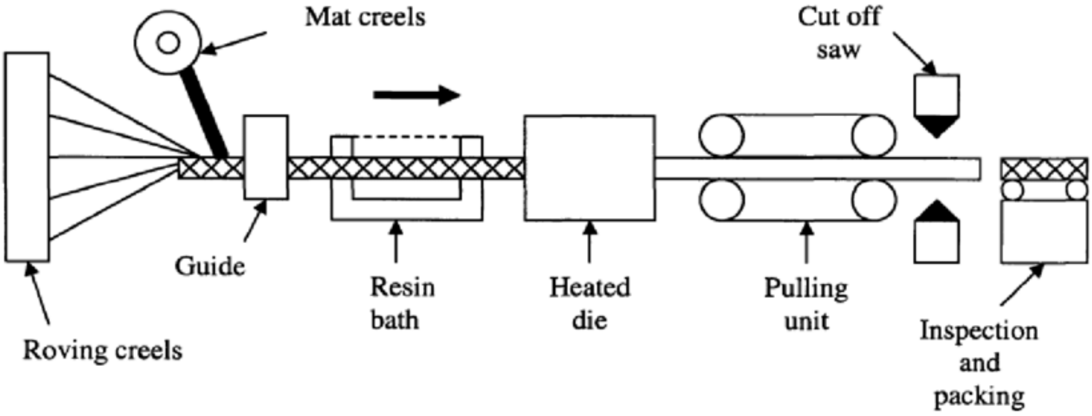


Figure 28. Pultrusion process.

At first, the reinforcement, usually glass rovings, is pulled from packages in a creel stand and gradually brought together and pulled into an open resin bath where the reinforcement is impregnated with liquid resin. The resin used must have a low viscosity and a long life.

After emerging from the resin bath, the reinforcement is first directed through a preform die that aligns the rovings to the part shape and then guided into a heated constant cross-section die where it cures as it progresses through the die.

The curing process takes place from the outside of the part toward the interior.

Finally, the composite part emerges from the die as a fully cured part that cools as it is being pulled by the puller mechanism. Then, the part is cut to the required length.

The main advantages of the pultrusion process are the low production cost as it is a continuous process. In addition, it is a simple and automatic process but at the beginning of the process it requires a lot of manpower and time.

This process has the disadvantage that it is limited to the production of shapes with a constant cross section and that the result of the pieces may have high porosity exceeding that allowed for structural applications.

### *1.6.1.6. Filament winding process*

The filament winding process consists of impregnating the resin fibres while they are wound on a rotating mandrel at the desired angle as shown in the Figure 29. [22]

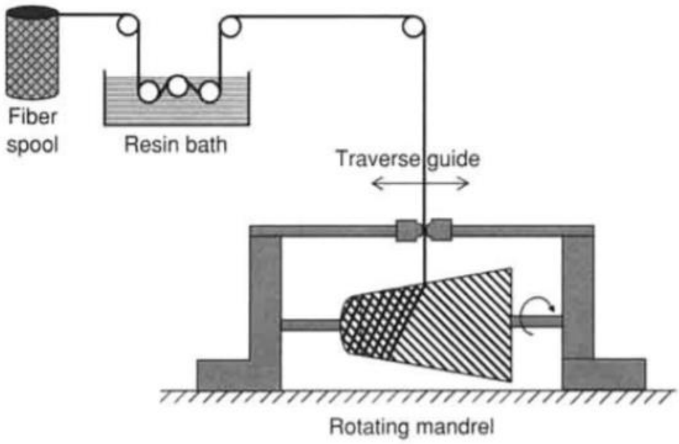


Figure 29. Filament winding process.

This process is used for the manufacture of tubular parts and has the advantage that it can be automated to make high volume parts in a cost-effective manner.

Filament winding is the only manufacturing technique suitable for making certain specialized structures such as pressure vessels.

### 1.6.1.7. Resin transfer moulding process

The resin transfer moulding (RTM) process also known as liquid transfer moulding offers the production of structural and complex parts cost effectively in medium volume quantities using low cost tools.

In the RTM process, a preform is placed in the mould cavity forming the “skeleton” of the structure, so that one half of the mould is attached to the first half and stays together.

Then, using dispensing equipment, a pressurized mixture of the thermosetting resin is pumped into the mould. After completion of the mould filling, the time curing cycle is applied at the temperature required to complete the part cure.

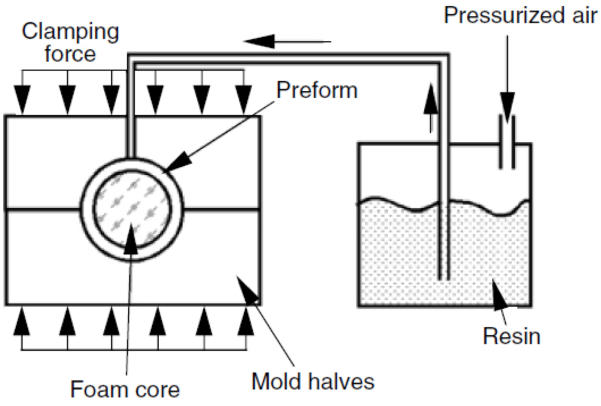


Figure 30. Resin transfer moulding process.

Finally, after the part has cured, it is removed from the mould.

With this technique, the production of structural parts with a good surface finish on both sides of the part is achieved. Also, this process is suitable for high-volume production of complex or thick composite parts and it has a low hardware and maintenance costs, this means, it is a cost-effective process.

This technique is used in some applications as military, aerospace, transportation, marine, and infrastructure products.

## 1.7. Cross-linking polymers. Curing

As we have commented in the section 1.5.1, polymeric matrix composites are divided into two groups: thermosets and thermoplastics.

In the case of thermosets, during the polymerisation process, the links between chains are created by chemical cross-linking reactions, also called curing. These cross-links can bind many polymer chains into a single three-dimensional network as shown in the Figure 31.

*Figure 31. Crosslinking of thermoset molecules during curing.*

The higher the number of crosslinkings the more rigid and thermallystable the materials will be. Cured thermoset resins may soften when heated but do not melt or flow. They generally have a higher resistance to heat than the thermoplastics.

Curing is defined as an irreversible reaction process in which chemical covalent cross-links are formed that are thermally and mechanically stable. Curing thus plays an important role in achieving the final mechanical properties and chemical resistance of the material.[32]

In other words, during the curing stage of the material, the transformation of the initial liquid state of the polymer resin before the manufacture of the composite to the final state of a solid matrix takes place. Two types of resins are used during the manufacture of the composite material: a primary resin or matrix, the most commonly used are unsaturated polyester and epoxy, and a secondary resin or hardener, generally the most common include peroxides or amines.

Depending on the composition of the resin and the hardener used, the cure can be done at both elevated and ambient temperatures[33].

When an optimal cure is achieved it results in a perfectly cross-linked polymer network, leading to an increase in the Tg glass transition temperature, temperature at which a polymer changes from a rigid and brittle state to a soft and malleable one, and the mechanical properties of the material.

It is therefore of particular interest to know the factors on which the glass transition temperature (Tg) depends. Tg depends on different factors such as resin molecule composition, curing time, curing agent, temperature and crosslink density [34].

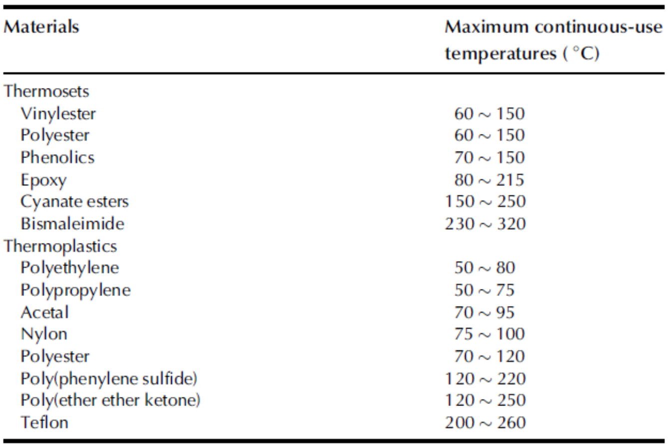
When curing is complete, there is a drastic increase in molecular weight, to a value that is virtually impossible to measure. Thermal properties such as melting point and glass transition temperature (Tg), on the other hand, no longer make sense since the polymer degrades before reaching either of these temperatures.

This is not the case for thermoplastics. In this case, a compromise between molecular weight and processability must be reached in order to obtain acceptable thermal and mechanical properties. Even so, they have an advantage over thermosets in that once they are melted, they can be easily shaped and therefore, depending on the type of matrix used, the characteristics of the final composite material will vary.[35]

The shrinkage stresses generated during the polymerization process, which is an exothermic reaction, and the thermal stresses caused by the differences between expansion coefficient of the matrix and the reinforcement, can affect the micro-voltages of composite materials. The stresses caused by the contraction of the polymer can be sufficient to produce micro cracks during the reticulation.

One of the critical factors in the performance of all polymeric matrices is the maximum temperature at which they can be used in service conditions. This value is usually characterized by the glass transition temperature or the thermal distortion temperature (HDT).

Maximum continuous-use temperatures of the various types of thermoset and thermoplastic resins are shown in the following Figure 32.



| Materials | Maximum continuous-use temperatures (°C) |
|---|---|
| Thermosets | |
| Vinylester | 60 ~ 150 |
| Polyester | 60 ~ 150 |
| Phenolics | 70 ~ 150 |
| Epoxy | 80 ~ 215 |
| Cyanate esters | 150 ~ 250 |
| Bismaleimide | 230 ~ 320 |
| Thermoplastics | |
| Polyethylene | 50 ~ 80 |
| Polypropylene | 50 ~ 75 |
| Acetal | 70 ~ 95 |
| Nylon | 75 ~ 100 |
| Polyester | 70 ~ 120 |
| Poly(phenylene sulfide) | 120 ~ 220 |
| Poly(ether ether ketone) | 120 ~ 250 |
| Teflon | 200 ~ 260 |

*Figure 32. Maximum continuous-use temperatures for various types of thermoset and thermoplastic resins.*

Thermoplastic resins can be amorphous or partially crystalline. The latter usually have higher HDT and greater resistance to solvents.

Thermosetting resins are amorphous and differ greatly in their Tg and resistance to solvent attack. A classification of thermoset matrices can be made, depending on the temperature of use.

During curing, the precursor resins of thermoset matrices can undergo different polymerization reactions. We distinguish in this way:

- Addition polymerisation reactions, usually by means of radicals.
- Condensation polymerisation reactions of functional groups.

At the first group includes unsaturated polyester resins, vinylester resins or other double-bonding systems. They generally have short curing times due to the high speed of radical polymerization.

On the other hand, the second group includes resins such as epoxies and phenolic resins.

In general, epoxy and polyester resins cover a wide group of chemical compounds and therefore a great variety of physical and mechanical properties.

### 1.7.1. UV-curing composites

UV-curable resins were introduced in the 1960s. But their use in composite materials was not very successful compared to heat-cured materials because of the ability of the latter to form very thick parts, as well as their potential for cross-linking with glass or carbon reinforcements.

The first UV-curable resins faced the problem of obtaining an achievable part thickness due to the restriction of the distance at which UV light could penetrate the laminate in high thicknesses and stimulate curing. So, the final curing of the part only occurred on the surface and not on the inside of the part.

Later, with the introduction of the photoinitiators, the technique of UV curing re-emerged, encompassing its use in new applications and gaining territory over conventional curing options.

The UV light curing technique consists of a process of curing the liquid material when exposed to UV radiation.

It is a low temperature process as no heat is required and it is a high-speed process. Two components are used in the curing stage, one is the photoinitiator and the other is the adhesive resin.[36]

The photoinitiator plays a very important role, it is responsible for absorbing the UV radiation that reaches the material. Thus, when UV light strikes the surface of the material it will undergo a chemical treatment responsible for the curing of the adhesive used, thanks to the polymerization reaction.

Moreover, one of its advantages is that it is defined as an energy-efficient process, in which energy is invested only in the curing reaction and not in heating as in the case of the heat-curing process.[37]

Another advantage of the UV curing process over thermal drying methods is that the time and therefore space required for curing is significantly less than with thermal drying methods.

Furthermore, because the process depends on UV light to initiate cross-linking of the molecules, no solvents are evaporated and the substrate is not significantly heated.

Curing with UV light depends on the collision of photon molecules. To achieve a successful result, a number of factors must be taken into account:

- UV light, since for the photoinitiator to react correctly it must be exposed to UV light with its correct surface intensity and wavelength. Otherwise, the result would not be adequate as the chemical reaction does not occur completely. Hence, the two most important characteristics to define UV light are intensity and wavelength.
  Although there are really four key factors for UV lamps: UV radiation (or intensity), spectral distribution (wavelengths) of UV radiation, UV energy (integral of radiation and time) and infrared radiation.[38]

- The difficulty and ease of photon projection also depends on the type of material as the optical properties of the curable material (polymer resin) and the characteristics of the UV lamp must match to produce efficient curing.

There are several ways to characterize the material: Spectral Absorbance, Optical Density, Infrared Absorptivity, Reflectance and Scattering, Diffusivity.[37]

Spectral absorbance refers to the relative energy as a function of the wavelength absorbed in the material at increasing depths. So, the greater the energy absorbed near the surface, the less energy is available at deeper levels of the material. This fact does not vary with the wavelength.

Like absorbance in the sense that it combines factors of "opacity" and thickness of a film we have the optical density which includes the light attenuation effects of absorbance and scattering. This value is expressed as a single number rather than a spectral distribution.

On the other hand, we have reflectance and scattering which is defined as the energy of light, which is "redirected" by or into a material rather than being absorbed. This phenomenon is typically produced by the substrate material and/or the pigments in the curable material which reduce the amount of UV energy available at lower depths. However, they improve the curing efficiency at the surface level.

We also have diffusivity, which is a thermodynamic characteristic that combines specific heat, conductivity and density to give us the ability of a material to "diffuse" heat input.

Finally, the radiant energy (IR) of the UV lamp is the main source of heat at the surface so that excessive temperature increases will affect the process and therefore the curing reactions. This characteristic is called infrared absorptivity.

Today, the number and variety of applications for UV-curable inks, adhesives and coatings continue to expand at a rapid pace, posing new design challenges to increase curing efficiency, speed and especially the physical properties of the final cured material.

One application where UV curing has been very successful is in the curing process of polymeric matrix composite materials where epoxy or ester vinyl type resins are typically used.

Other applications to which this type of curing has been largely adapted are paint and coating (on wood, paper, plastic and metal), decoration and assembly of a wide variety of products.

### 1.7.2. Post-curing

In our case, during the curing process, the epoxy resin is transformed from a low molecular weight material to a high cross-linking polymer system and these interlocking chains are the ones that confer the characteristics of rigidity and resistance.

However, in some cases, the epoxies used must be treated with post-curing by heat to improve their resistance since they must reach a certain temperature in order to complete the chemical reaction and optimize their properties.

There are several parameters that define the post-curing process: temperature and time, but also the time between initial curing and post-curing and the temperature profile gradient are paramount.

During post-curing at temperatures above the Tg of the polymer, the monomers of the resins have a better capacity to polymerize due to the increased mobility of the molecular chains and the neutralization of the immobilization of the residual monomers in the polymer. Generally, Tg increases with increasing post-curing temperature, but without exceeding the curing temperature.

The main advantage of post-curing as an independent operation, even in the case of parts already cured, is that it increases the glass transition temperature and improves properties such as: resistance to chemical agents, thermal stability, dimensional stability, electrical resistance and resistance to humidity.

Especially, epoxy resins behave better with post-curing, as it increases cross-linking, having a very important role in increasing the adhesion of the epoxy coating system.

There are also other types of polymers in which properties are affected by post-curing processes. For example, in polyamide polymer films, the tensile strength and elongation of the basically rigid film can be improved by post-curing at 360-370°C for one hour.

Studies have also been conducted on the effects of post-curing on glass fibre reinforced polymers (GRP). Post-curing in this type of polymer has a small effect on water absorption and a significant influence on reducing solubility. [39]

## 1.8. End of life

### 1.8.1. Situation of world waste production

Population growth, economic development and consequently the urbanization of territories are closely linked to the generation of waste.

As the population of cities increases, they thrive on economic growth by offering more products and services, which are eventually transformed into waste for treatment or disposal.

According to the World Bank's What a Waste 2.0: A Global Snapshot of Solid Waste Management, the waste generation worldwide appears in the following Figure 33[40]:

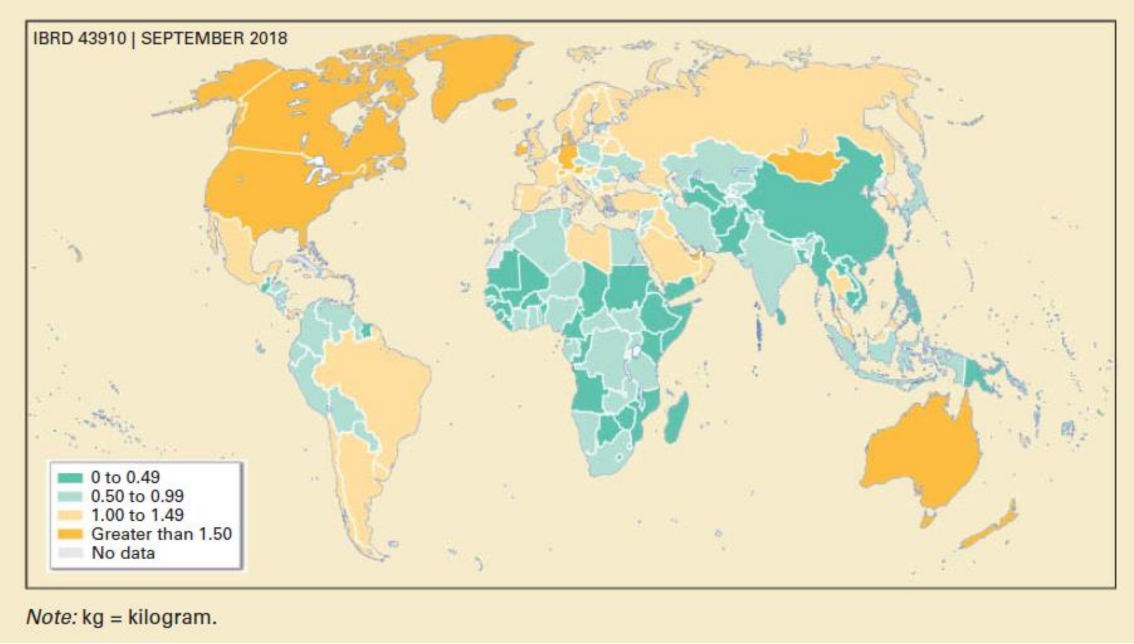


*Figure 33. Waste Generation Worldwide per capita.*

Moreover, according to this report, if action is not taken to reduce waste production urgently, global waste is predicted to grow by 70 per cent from current levels by 2050 as a result of rapid urbanization and rising populations around the world (Figure 34).

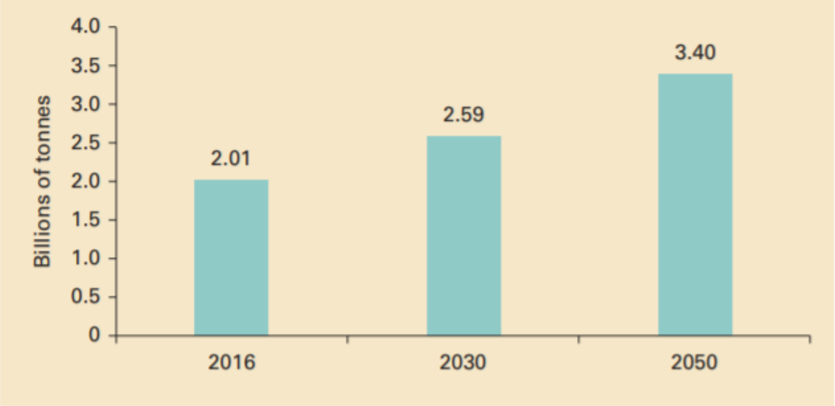


*Figure 34. Projected Global Waste Generation.*

### 1.8.2. End of life of composites

Due to the continued preference for composite materials, the waste generated has also increased, hence the need for recycling methods. In addition to the environmental impact that these wastes cause, legislation and regulations imposed in a restrictive manner by the European Union have encouraged more developed countries to give research into the recycling of these materials a chance [41].

In this way there is a hierarchy of EU routes for dealing with composite waste (Figure 35).

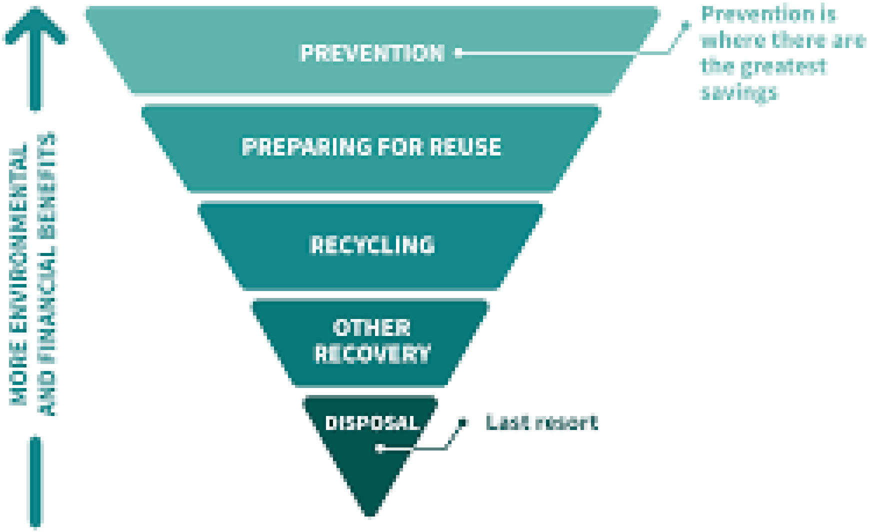


*Figure 35. Waste management categories hierarchy.*

The hierarchy that exists in descending order of convenience is as follows [42]:

- Prevention

The design stage is a critical step in determining the degree of circularity of any product. During the design of the product, an attempt should be made to design it in such a way that after use it will have future applications for reuse or re-use.

In addition, consideration should also be given to the EoL phase of the product, i.e. ensuring its recycling which is closely dependent on the material selected the material selection and combination, design for dismantling considerations, and material separation properties. This prevents the increase of waste from industrial cemeteries.

- Reuse and repurpose

Before considering the product unusable, trying to repair or treat it to give it a second chance or reuse it in other applications

- Recycling

This consists on turning waste into a new substance or product. Currently is becoming popular around the world as it succeeds in making new materials with good properties from recycled materials. In this way, the environment will be preserved.

- Recovery

We have the incineration of the waste within which there are three possibilities. In decreasing order, they are: with material and energy recovery, with energy recovery, without energy recovery.

However, this category includes the incinerations that involve the material or energy recovery.

Although it is very promising in terms of efficiency and profitability, this process is in the lowest positions in the hierarchy.

Therefore, it should be used only when the value of the composite materials is no longer suitable for any other application.

- Disposal

Landfilling has been the most common way of handling waste during the time. This option consists on throwing the waste to a specific place and unloaded there.

Landfilling and incineration without energy recovery translate into an absolute loss of resources and is, therefore, preferably to be avoided.

In this hierarchy established by the European Union, we can see that the recycling of disused material is the primary and previous option to the elimination of waste via incineration or landfill.

### 1.8.3. Recycling of thermoset composites

In order to carry out proper recycling it will be necessary to focus on the current technologies available, the environmental and socio-economic impact that can be generated, as well as the mechanical properties of the recycled materials and their subsequent application.[43]

In short, there are two motivations associated with the recycling of composite material waste. The first we have mentioned above is the environmental problems involved in its existence and the second, and no less important, is the cost of producing virgin fibres for the manufacture of new composite materials.

There are basically three possible ways of recycling composite waste management: chemical, mechanical and thermal recycling.

However, new technologies such as the use of high voltage shredding (HVF) are helping to introduce a more sustainable, efficient and rational form of recycling (Figure 36).

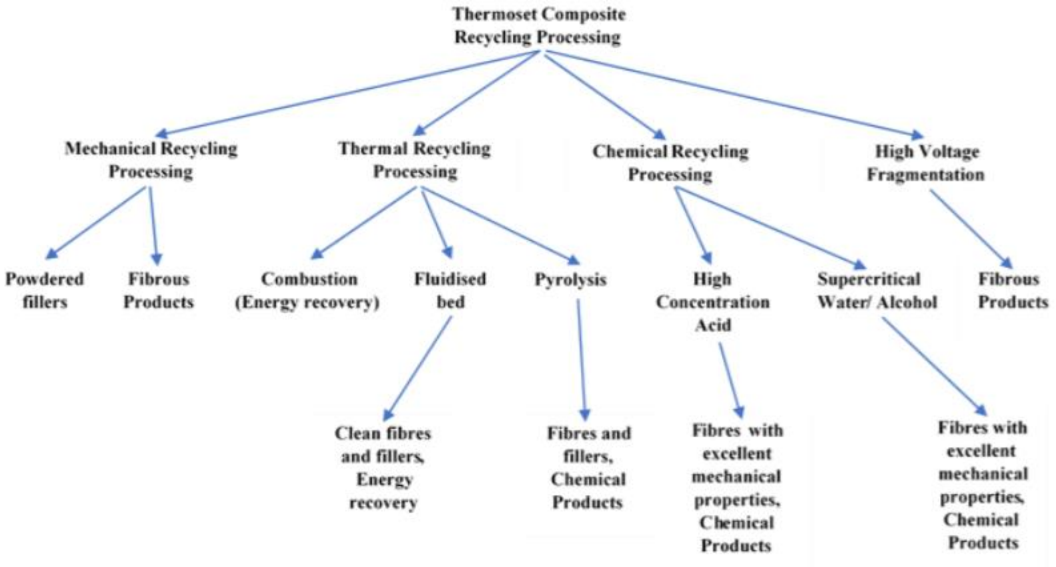


*Figure 36. Ways of recycling Thermoset composite.*

As this work will consist of providing a second use for recycled GFRP materials, we will briefly explain the different recycling processes of existing FRP composite materials.

Nowadays, due to the fact that society is becoming aware of the importance of respecting the environment, studies and advances in clean energies have increased, highlighting in particular, wind energy, which plays a leading role in the manufacture of waste FRP materials so that the quantities of used FRP materials have increased. Hence the need to identify and develop possible solutions to give them a second life and contribute to the development of a circular economy.[44]

In order to achieve a correct recycling process, three main objectives must be taken into account: recycling in a way that emits as little pollution as possible to the environment, an economic process and also it does not excessively damage the final material for reuse.

Therefore, numerous studies and patents have been carried out and published on the possible ways to recycle composite materials. At present, we find chemical, thermal and mechanical processes[45].

#### *1.8.3.1. Thermal*

Thermal recycling consists of the use of heat to decompose waste composite material. There are different types of thermal processes that differ according to the degree of energy and material recovery: pyrolysis, fluidized bed and combustion.[42]

The thermal recycling process of combustion consists of the burning of compound waste in the presence of oxygen. The different calorific values available depend on the type of polymer and, for example, the calorific values of glass-fibre reinforced composites depend on the type and proportion of polymer used. [43]

In this type of process, energy recovery from the combustion of fibre-reinforced composite waste is very feasible. The remains of non-combustible materials can be disposed of in landfills or used, for example, as filler for minerals commonly used in composites containing minerals that can be incorporated into cement.[42]

Another thermal recycling process is pyrolysis, a process that allows the recovery of the fibre and matrix in the form of ash.

During the pyrolysis process, the composite material residues are subjected to high temperatures in an inert atmosphere and in the absence of oxygen, causing the degradation of the polymer into gases and liquids of lower molecular weight.

Hence, the products obtained after pyrolysis are gases, oil, carbon, fillers and fibres. This is its main advantage over mechanical recycling.

A scheme of the pyrolysis process is shown in Figure 37.

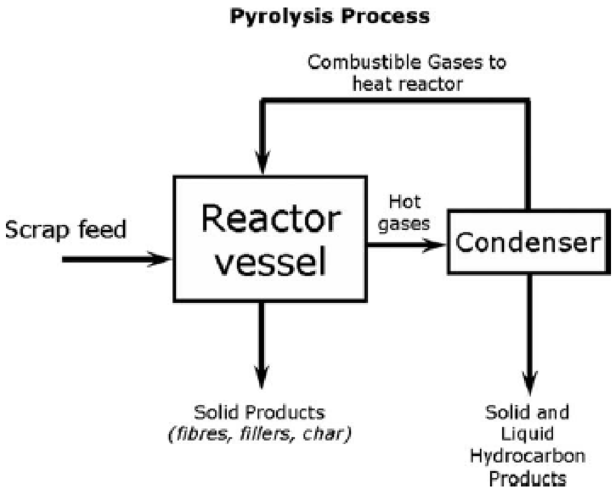


*Figure 37. Pyrolysis process.*

However, the main disadvantage of this type of thermal recycling is that the high temperatures required to carry out the process affect the mechanical properties. Hence, new studies are focused on the use of catalytic pyrolysis [43,46] where the use of a catalyst allows working at lower temperatures thus avoiding damage to the mechanical properties of the material. In addition, a high investment is required and its operating costs are high. [47]

Another thermal process that exists for the recycling of composite material waste is oxidation in fluidized beds. This process only allows the recovery of the fibre by combustion of the polymer matrix in a hot, oxygen-rich flow. Unlike pyrolysis, in this process the recovered fibres are clean showing low surface contamination by carbon deposition; however, damage to the mechanical properties of the material still occurs.[48]

The great advantage of oxidation in a fluidized bed is that it allows the recycling of mixed or contaminated composite materials such as paints or foams [47]

The following Figure 38 shows a general diagram of the oxidation process in a fluidized bed:

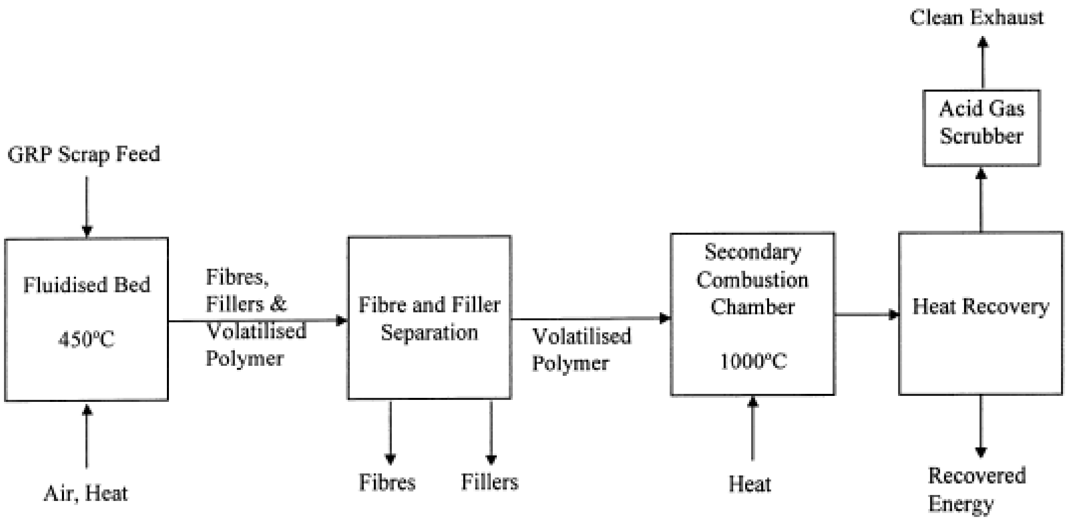


*Figure 38. Fluidised bed thermal recycling process.*

In this diagram it can be seen how the polymer of the composite material is volatilized releasing the fibres and fillers that are suspended in the gas stream. Subsequently, these are separated from the gas stream and passed into the chamber where secondary combustion takes place at high temperatures and where the complete oxidation of the polymer takes place. Finally, energy recovery from the combustion products takes place.[42]

### *1.8.3.2. Chemical*

Chemical treatment is generally used for the recovery of thermoplastic waste. This type of recycling, also called solvolysis, consists of breaking the dividing bonds present in the spine of polymers of staggered growth, which leads to chemical depolymerization, by means of soluble processes such as glycolysis, hydrolysis and aminolysis. [49]

This type of recycling offers many possibilities because it has a wide range of solvent, temperature and pressure options.

For example, processes such as glycolysis or hydrolysis are used today to decompose epoxy resin into its original monomers for the manufacture of raw materials [50].

In order to carry out the breakage of the matrix of the composite materials it is necessary to use reagents. The most used solvents and that better results have been obtained have been the alcohols, the acetone and the supercritical water.

However, within these three types of solvents used, the use of alcohols and water is particularly noteworthy, as they have high availability and low toxicity, as well as being more environmentally friendly. In particular, the use of supercritical water as a solvent is the most promising technology, as it achieves the recovery of fibres and resins without major repercussions on their mechanical properties.[47]

A supercritical liquid is neither a vapour nor a liquid but is one that is at a pressure and temperature above its critical point, which makes it behave as a hybrid between a liquid and a gas, i.e. it can dissolve substances as a liquid (solvent) and diffuse as a gas.[51]

Thus, when a liquid or solvent is in the supercritical or near-critical region, the dielectric constant is significantly reduced, and the hydrogen bonding essentially disappears. [52]

Furthermore, when used under supercritical conditions they possess a combination of characteristics such as high mass transfer coefficients and high diffusivity as well as low viscosity. In this way, they are suitable for example for recycling CFRP composite materials by degrading the resin without the fibres being affected to any great extent.

Compared to thermal recycling, the use of a chemical treatment means working at lower temperatures to be able to degrade the resins, which contributes to less degradation of the fibres of the composite material to be recycled.

However, this type of recycling has some disadvantages since the solvolysis uses some salts or other modifying components that damage the fibres and can be contaminating. In addition, the investment and operating costs are high.[43]

#### *1.8.3.3. Mechanical*

With regard to the mechanical recycling techniques available for thermoset FRP composites, mechanical grinding is the only method used in industrial-scale processes[43].

The mechanic's recycling process consists of the collection of small particles and fibres through crushing, grinding or grinding processes.

To carry out this technique, three steps[48] are usually performed:

- Reduction of the initial size of the waste material by crushing it into pieces between 50-100 mm in size.

- Reduction of the final size in jaw crushers, hammer mills or knives where the waste material is crushed again to achieve a finer result ranging from 10 mm in size to particles of less than 50 micrometres.
- After grinding, the resulting material is classified and separated, the most commonly used technique being sieving despite the fact that it presents the problem of "fuzz-ball", an effect produced by the movement of the sieve and the fibres [53].

On an industrial scale, combinations of sieves and cyclones or air separators are made[54].

Finally, as a result of mechanical recycling, two types of recycling can be obtained, one type of recycling formed by the coarser particles that correspond to a greater quantity of fibre and on the other hand, another type of recycling with large percentages of the finer particles with a high quantity of resins and filling particles [55].

Compared to other recycling techniques, mechanical recycling has better environmental and economic advantages. Some of the advantages are that it does not cause any water pollution from chemical spills or air pollution from gas emissions. In addition, it does not require any high-cost or highly sophisticated equipment and finally, it allows its use on an industrial scale as it allows the processing of large amounts of waste at high throughput.

However, despite its advantages, there are some drawbacks such as safety problems due to the risk of ignition during the shredding stage. Another problem is that the value of the final material is not very competitive with virgin raw materials such as purchased glass fibres or calcium carbonate.[48]

## 1.9. Applications of composite materials

The use of composite materials is covering many sectors of engineering thanks to its advantages over conventional materials.

Once the desired composite material has been obtained, it must be driven through a series of steps to arrive at the final product to be used in each application.

The necessary steps to make the product complete are the following:

a) Conformation

This step corresponds to the design and moulding stage of the piece, that is, the shape and size of the composite material is changed until the desired one is achieved, generally under the action of pressure and heat.

b) Machining

In this step, the excess or desired material is removed. Drilling, turning, cutting and grinding belong to this category.

c) Assembling and fitting

This step consists of joining and assembling the different components. This is usually done using adhesives, by melting or mechanical fixing. This stage is the one that needs more time as well as being the most expensive. For this reason, in order to reduce costs, the integration of the parts is carried out.

d) Finishing

This final stage is carried out with the purpose of improving the aspect of the final product as well as providing a coating to the parts to protect them against environmental degradation and to avoid wear.

Composites are widely used in many applications as shown Figure 39. Such as the aeronautical and naval sector, in the manufacture of wind turbines, in construction, in fibre optic cabling, in prosthesis, etc.

*Figure 39. Applications of composites.*

In the automotive industry today, composite body panels have a successful track record in all categories from exotic sports cars to passenger cars and small, medium and heavy truck applications.

Because the automotive market is very sensitive to economic costs, carbon fibre composites are not yet accepted due to the high cost of the material, however glass fibres are used as the main reinforcement.

The civil structures and construction industries are the second largest consumer of composite materials in the market. For example, the use of glass and carbon reinforced polymers for bridge applications results in reduced installation, handling, repair and life cycle costs, as well as improved corrosion and durability. Furthermore, within this industry, some columns are being wrapped by glass/epoxy, carbon/epoxy and aramid/epoxy showing great potential for certain applications.[56]

Therefore, when designing the hulls and decks of boats in nautical production, composite materials are widely used thanks to their low maintenance cost compared to steels.

Moreover, the aerospace industry was one of the first to realize the benefits of composite materials. Planes, rockets and missiles fly higher, faster and further with the help of composite materials.

For example, materials such as glass, carbon and Kevlar fibre with the right composites have been used for the design and manufacture of aerospace parts.[9]

In the aeronautics sector they are used due to their great lightness and mechanical resistance, contributing to a reduction in fuel consumption, since nowadays the use of carbon fibres can reduce the weight of an aircraft by 20%.

Finally, as we mentioned above, in the wind sector composite materials are used primarily for the manufacture of wind turbine blades (Figure 40). As we have seen in this work, the blades are generally manufactured with epoxy resin reinforced with fibreglass.

*Figure 40. Turbine blades composed by glass reinforced polymer composite.*

On the other hand, within the same energy industry, there are the mini wind turbines used for the generation of electric energy in many fields and that we can find in private homes, isolated telecommunication stations, agricultural irrigation and recreational boating stations. They have the advantages of easy installation, low maintenance, durability and reliability.

## 1.10. Barriers in Composite Markets

Despite the countless advantages of using composite materials, they face the great problem of the end of life of the product due to its difficult recycling stage.

In addition, recycling of composite materials sometimes presents a big problem when dealing with a high-volume market such as the automotive industry where its production of parts reaches the amount of millions per year.[57]

Another major barrier to the use of composite materials is the high initial cost in some cases compared to conventional materials. In general, the cost of processing composites is high, especially in the handling process.

Therefore, when this problem arises, industry considers that despite the effectiveness of the composite material over its lifetime it does not become a profitable activity by inhibiting research into new materials.

Because of this problem and thanks to new government regulations and environmental awareness, the use of composites has become a concern and poses a great challenge for recycling. As a result, numerous studies have emerged that seek more sustainable environmental alternatives that give a second chance to those wastes or disused products whose end of life are being their corresponding cemeteries.[58]

This is where the objective of this project comes in, the re-use of fibreglass from the wind energy sector for the manufacture of new materials.

### 1.10.1. Reuse of fibreglass from the wind sector for the manufacture of new materials

As mentioned above, the main problem in the wind energy sector is the management of those components manufactured from composite materials such as blades that are in disuse or are reaching the limit of their useful life.

Composite materials, in this case fibreglass reinforced with plastics, present problems when it comes to finding the most optimal recycling process possible, since this type of material has the disadvantage of being recycled.

The wind industry, as we have mentioned before is currently growing. Moreover, the International Energy Agency predicts that the wind industry will continue to grow and supply between 15% and 18% of the world's electricity by 2050 [59] and with it the increase in the number of turbines manufactured. However, those turbines installed at the end of the 80s and beginning of the 90s are reaching their final life cycle and those manufactured after the year 2000 will reach the end of their lives in the very near future.

It is considered that the end of life of a wind turbine takes place after reaching 20-30 years so that at that time they cease to fulfil their function due to fatigue or failure or simply fail to meet the desired expectations[60]. From there, the need to find answers to the question of what to do with them emerged.

The main idea that has emerged in today's society is the recycling of turbine blades[61]. Thus, according to statistics and studies, it is predicted that by 2034 around 225,000 tons of rotor blade material will be recycled annually worldwide[62].

This is the context in which this project is being developed, the manufacture of a new composite material from the recycled fibre of the wind turbine blades to a composite material that achieves the best properties desired in the materials industry for subsequent use in other applications.

# 2. MATERIALS

## 2.1. Re-manufacturing composite

### 2.1.1. Epoxy resin

In this work an epoxy resin based on bisphenol-A (epichlorhydrin) containing 1,4-bis(2,3-epoxypropoxy) butane, a difunctional reactive diluent, has been used for the manufacture of the new composite material. Its commercial name is AralditeBY158 and it has been supplied by Huntsman Corporation (Figure 41 and 42).

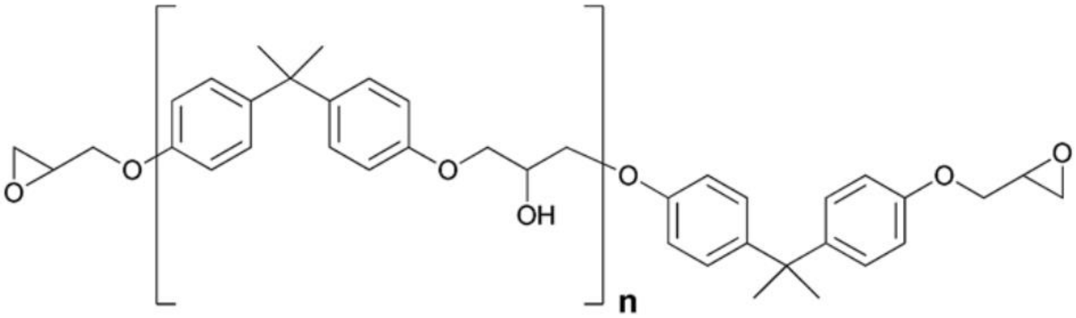


*Figure 41. Chemical structure of epoxy resin based on bisphenol-A (epichlorhydrin).*

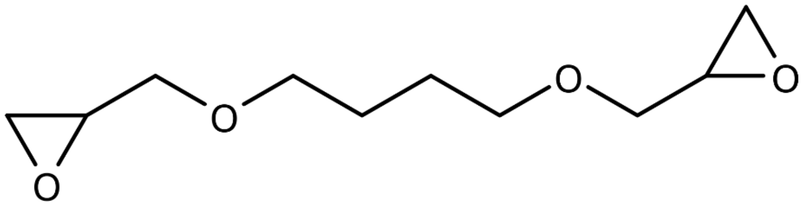


*Figure 42. Chemical structure of 1,4-bis(2,3-epoxypropoxy) butane reactive diluent.*

### 2.1.2. Curing agent

To modify the viscosity and processing of the system, AralditeBY158 was combined with the curing agent commercially called Aradur21, which is a trimethylhexane-1,6diamine component (Figure 43). It was also supplied by Huntsman.

This curing agent shows good colour stability, low viscosity as well as good resistance to aqueous, neutral and alkaline solutions. It offers good mechanical properties after optimal curing.

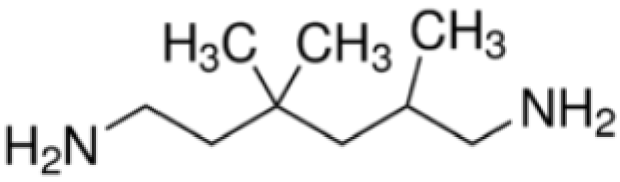


Figure 43. Chemical structure of trimethylhexane-1,6diamine curing agent.

### 2.1.3. Recycled reinforcement

The recycled reinforcement used in this work for the manufacture of a new composite material has been provided by GAMESA S.p.A. This material comes from the disused blades of the wind sector and is composed of virgin glass fibres and commercial resin.

This reinforcement is composed of fine dust and fibres of a size less than 4 mm. Figure 44 shows an image of the powder elaborated through ImageJ software from the SEM.

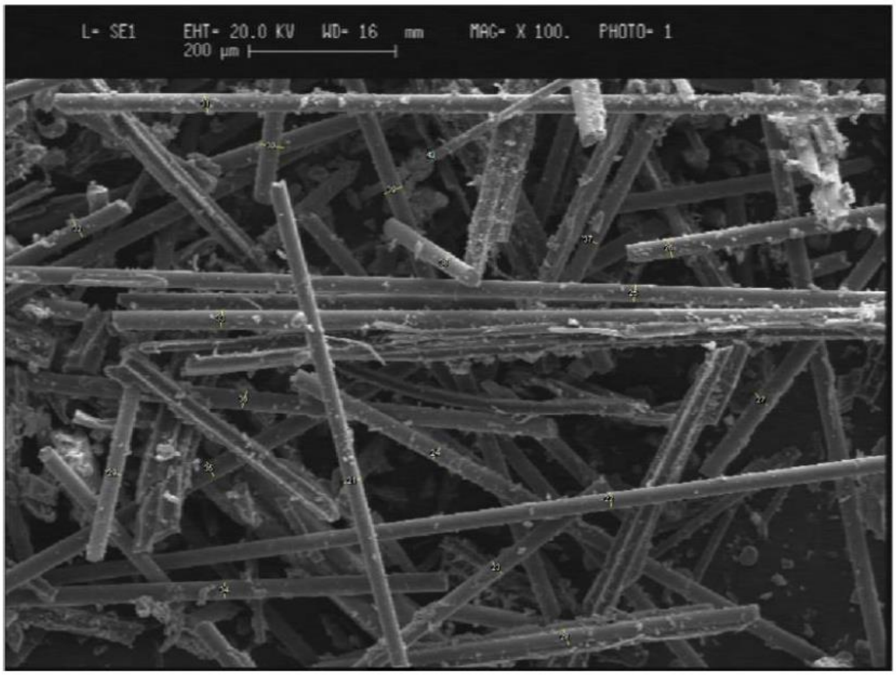


Figure 44. ImageJ fibre on a SEM picture.

## 2.2. Coating solutions

For the coating of remanufactured composite, different types of solutions have been manufactured that will act as coating resins.

The reagents used were the commercial epoxy resin AralditeBY158 and the curing agent Aradur21, which were used to manufacture the new material composite recycled.

A cationic photoinitiator, 4,4’-dimethyl-diphenyl-iodonium hexafluorophosphate designed for commercial UV curing systems called Omnicat440 also has been used. (Figure 45).

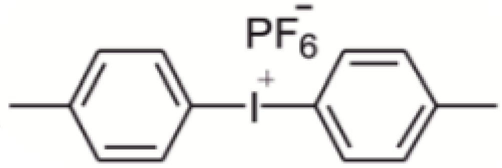


Figure 45. Chemical structure of 4,4’-dimethyl-diphenyliodonium hexafluorophosphate.

Some anhydride compounds are used such as succinic anhydride Figure 46 and phthalic anhydride Figure 47.

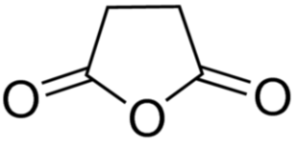


Figure 46. Chemical structure of succinic anhydride.

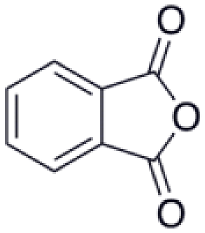


Figure 47. Chemical structure of phthalic anhydride.

Different solutions were prepared with different compositions.

# 3. METHODS

## 3.1. Mechanical recycling of glass fibres (recycled composites from wind industry)

Firstly, to obtain our recycled fibre, a standard mechanical recycling process carried out by STIIMA-CNR (Istituto di Tecnologie Industriali e Automazione-Consiglio Nazionale delle Ricerche) has been used.

The composites from which our fibre comes were subjected to a size reduction procedure from 10 mm to 80-100 µm using an Erdwich single shaft shear shredder, model M600M-400, shown in Figure 48.

*Figure 48. Erdwich single-shaft shredder model M600M-400.*

To achieve the right size of fibre, a second fine grinding was carried out using four different grids through a Retsch cutting mill, model SM-300 as shown in Figure 49.

*Figure 49. Retsch cutting mill, model SM-300.*

The result obtained was fibre particles with a dimension less than 4mm, around 2mm as shown in the following Figure 50:

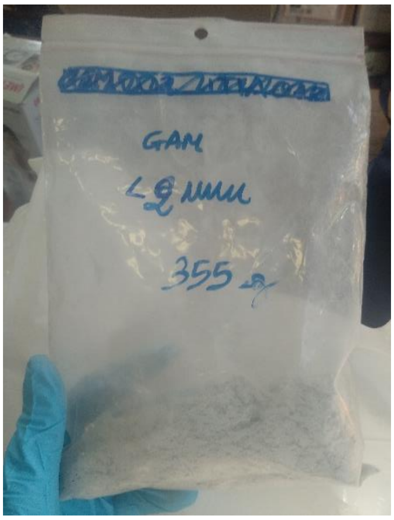


*Figure 50. Recycled fibre.*

## 3.2. Resin preparation

For the preparation of the resin of our recycled composite samples, certain quantities of AralditeBY158 epoxy resin and Aradur21 with 28 wt.% curing agent were used.

Once the appropriate quantities were measured on the laboratory balance according to the chosen formulation, both components were properly mixed in a beaker with a spatula.

During mixing the transition from light to opaque colour could be observed and after stirring the transition from opaque colour to light odour was experienced again as at the beginning indicating that it was ready for use in the next step.

## 3.3. Mixing

Firstly, the recycled fibre was placed in an oven for one night at a temperature of approximately 50ºC with the aim of drying it completely to remove the trapped gases and water, thus improving the adhesion of the fibre matrix.

To create the final mixture of our composite material, the recycled fibre was weighed in the right proportions to the amount of resin. The proportion of recycled fibre used in the resin mixture of AralditeBY158 and Aradur21 was 60%.

Once weighed, it was mixed with the previously prepared resin solution and left in agitation for approximately 15 minutes until a homogeneous mixture was obtained, so that the recycled fibre used was totally impregnated with the resin.

To achieve a homogeneous mixture, a mechanical stirrer as shown in the Figure 51 was used, increasing its speed gradually from 50 rpm to 250 rpm.

Figure 51. Mechanical stirrer.

## 3.4. Vacuum application

The resulting mixture of resin and fibre was subjected to a low vacuum level during approximately 15 minutes to remove any excess air and resin, thus preventing the formation of future bubbles in the following steps.

The system used was composed of a flask, a glass container, a filter with a porous septum, a silicone stopper and a lab clamp as shown in Figure 52.

Figure 52. Vacuum system used.

## 3.5. Moulding

The mixture of recycled fibre and resin was placed between two polymethyl methacrylate (PMMA) sheets, acting as a mould with the help of a roller (Figure 53). Metallic sheets were also used as mould.

This procedural step was very important to carry out correctly in order to avoid the formation of holes on the surface and to achieve a homogeneous thickness to guarantee the best result of the remanufacturing compounds.

*Figure 53. Craft roller and PMMA sheets.*

Once the moulding was done, the mould was placed in the press as shown in the Figure 54 for 24 hours at room temperature producing the compression moulding and thus avoiding contact between the mixture and moisture in the air.

*Figure 54. JBT Engineering hydraulic press.*

The material chosen for the mould was PMMA as it is a material which, after preliminary and qualitative adhesion tests, was the best suited for removing the final material after the compression treatment without causing any damage.

## 3.6. Curing and post-curing

After the compression moulding of the sample in the hydraulic press for 24 hours, with the curing taking place at room temperature, the final mould material was removed and the post-curing treatment was carried out.

In this project, the thermosetting epoxy resin has been used for the manufacture of the composite material samples, since these according to the studies are the most used due to their excellent wettability and strong adhesion to the fibre[63].

In our composite samples, at molecular scale, the epoxy-amine reaction involves the opening of the epoxy ring by reaction with a hydrogen amine.

It is observed that the initial curing stage is largely dominated by the primary amine reaction as the secondary amines are sterically obstructed[64].

Sometimes, a single stage of curing of the composite material is not enough to achieve the most optimum properties of the final material. For this reason, in this project, after curing the sample at room temperature for 24 hours, it was decided to carry out post-curing by introducing the pieces into an oven for 1 hour at a temperature of 100 ºC.

So, thanks to this post-curing, the complete conversion of the secondary amines is ensured.

## 3.7. Surface pre-treatments

Like any industry, the materials industry has its disadvantages, hence the extreme importance of pre-treatment of numerous surfaces.

Some of the disadvantages that lie in this industry is obtaining a long life for adhesive joints in very severe areas of the surface of the materials, hence the need to use a pre-treatment that improves the bonding surface.

Therefore the main objectives of pre-treatment are as follows[65]:

- Maximize the degree of molecular contact reached between the substrate and the adhesive during the bonding operation.
- Ensure that the level of intrinsic bonding forces established through the interface are sufficient to achieve the required bond and service life.
- Obtain a specific surface topography on the substrate
- Promote hardening of the adhesive.
- Assist with the protection of the substrate surface prior to the bonding operation when dealing with metallic surfaces.

### 3.7.1. Abrasive paper

Before applying the coating solution, it is necessary to sand the entire surface, removing impurities and creating a surface suitable for the subsequent correct adhesion of the paint or solution. Once our piece has been well scraped, it must be cleaned in depth, avoiding plastic particles or dirt. This operation can be repeated several times, using finer and finer sandpapers, until the surface is ready.

In this case, it was used a P400 and P500 abrasive papers as shown in Figure 55.

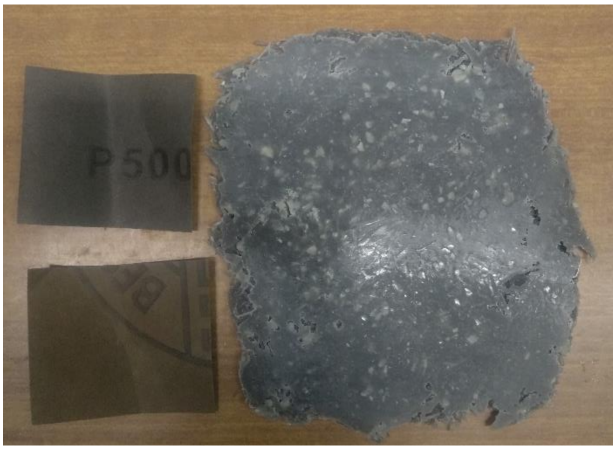


*Figure 55. Different types of abrasive paper as surface pre-treatment.*

### 3.7.2. Soap, water and 2-propanol

The cleaning of the surface of the part is very important. It must be clean, dry, and free of substances that prevent adhesion to the surface before causing problems. For example, a great enemy that could affect the result would be dust.

In this project our parts made from recycled fibre, after the sanding stage, have been washed first with water and soap and then with 2-propanol in order to remove any residue.

The 2-propanol, also called isopropanol is a highly recommended solvent for the removal of fats, oils and residues on all types of surfaces because it is a powerful diluent of non-polar compounds, lower toxicity and high volatility.

Finally, the parts have been dried using an ozone source.

### 3.7.3. Plasma treatment

Plasma technology has been used during this project with the aim of providing greater cleanliness of remanufactured composite samples by improving the subsequent deposition of our solutions during the coating stage.

This technology, as its name indicates, consists of carrying out treatments with plasma, a gas to which a large amount of energy has been applied so that positively charged ions and free electrons are created that also possess a large amount of energy allowing interactions to take place with the material to be treated while they move freely [66].

During the application of the plasma to the surface of our solid sample, the ions and electrons are precipitated on it and recombine giving rise to neutral atoms. In this way any residues on the sample surface are eliminated.

This technique as a surface treatment has the advantage that it does not use chemicals such as solvents, thus avoiding the storage and disposal of waste. [67]

Another effect for which this technology has been used is that the plasma activates the sample surface increasing the receptivity of the solid sample with the solutions used during the coating stage after the application of the plasma.

In this case, oxygen has been used as an oxidant to improve this receptivity, since air is the most economical.

There are different processes to carry out a surface treatment. During this project, the plasma chamber shown in the Figure 56 has been used.

*Figure 56. Plasma chamber treatment.*

The plasma is generated in a chamber at very low pressures where the sample is introduced. As the operating conditions are under vacuum, the installation consists of the plasma chamber, a vacuum pump and an external module [68].

## 3.8. Preparation of coating-solutions

The solutions used for the coating of the samples remanufacturing have been done in different compositions.

Firstly, solutions composed of AralditeBY158, Aradur21 and Omnicat440 were prepared. The latter was used in different percentages: 3% y 5%.

Later, due to problems in the UV-DSC measurement of the samples, the compound Aradur21 was replaced by an anhydride. The succinic anhydride was used and because of homogeneous problems this was replaced by phthalic anhydride.

## 3.9. Coating techniques

In order to protect the composite material and provide a high-quality finish, different types of solutions have been applied to act as resins on the surface of the material.

Before directly coating our samples with the solutions, coating tests were carried out on micro plain glass slides precleaned of 75x25 mm and a thickness of 0.96 to 1.06 mm by Corning Incorporated. Before coating, they were washed with soap and water and acetone and dried on an oven.

### 3.9.1. Brush

The first technique used for the coating of the samples was the deposition of our solutions on the surface using a brush. The results obtained were unfortunate as the final result was an irregular layer.

For this reason, it was decided to try it with another technique such as the use of the square metal piece using in primers or an airbrush.

### 3.9.2. Primer

In this case, the necessary instrumentation for a primer has been used. The primer is a preparatory coat that is applied to the surface of the materials before they are painted, ensuring better adhesion as well as providing additional protection to the material.[65]

In the Figure 57 appears the instrumentation used, a metallic square using the measure 1mils.

Figure 57. Primer instrumentation.

### 3.9.3. Airbrush

The best result for the coating process on the surface of our samples has been through the use of an airbrush, in particular the elite airbrush kit FE-183 by Fengda. Figure 58.

*Figure 58. Airbrush model FE-183 by Fengda.*

To avoid the minimum contamination during the coating stage, an ozone source installed in the laboratory has been used as a compressor. The pressure established during the coating of the pieces has been a pressure of approximately 2 bar.

This procedure has been carried out under a hood and with the necessary laboratory personal protection equipment such as goggles, gloves and safety mask.

## 3.10. UV-curing

After coating the samples with the solution through the airbrush were exposed under UV light for 10 minutes to achieve full cure.

## 3.11. Characterization techniques

The following sections will briefly explain the different characterization techniques used for the study of our recycled composite material.

### 3.11.1. Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermo-analytical technique that analyses how temperature changes the heat capacity (Cp) of a material. In a thermal cycle, the variation of the specific heat is directly linked to the variation of the enthalpy:

$$C_p = \frac{dH}{dT}$$

It does this by measuring the temperature-dependent variation in heat flow between the sample under investigation and that of a reference material while undergoing a controlled heating or cooling cycle.

This technique is generally used for the evaluation of polymer glass transition temperature and other thermal events corresponding to physical or chemical transitions in a sample that are shown in Figure 59.

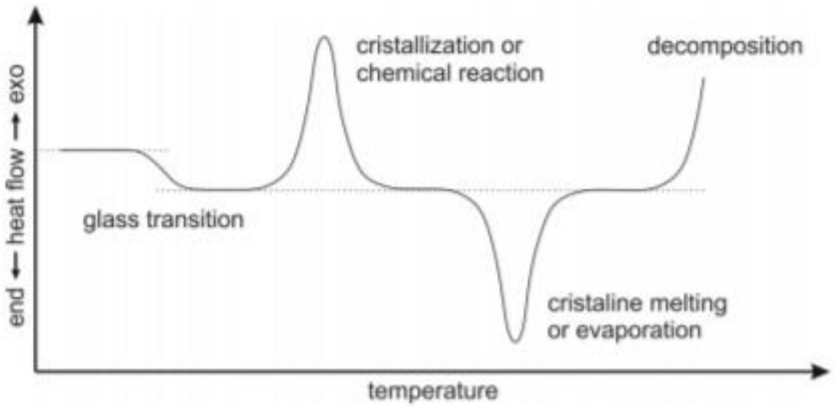


Figure 59. Thermal events in a DSC plot.

In this project, DSC analyses were performed on a DSC 823e calorimeter (Mettler-Toledo) as shown in the Figure 60, to determine the glass transition of cross-linked resins.

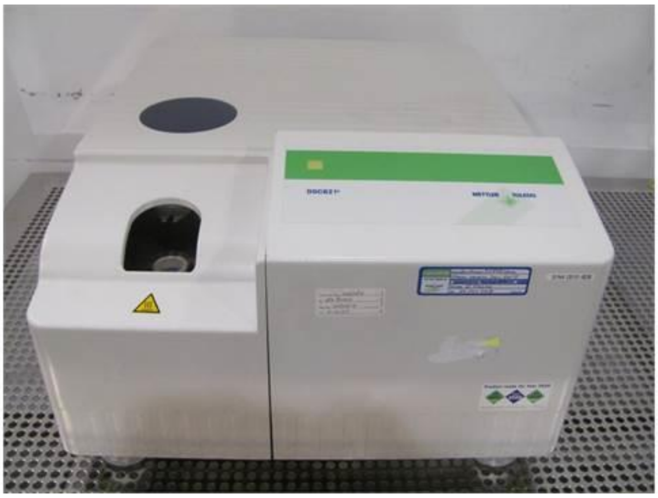


Figure 60. DSC 823e calorimeter (Mettler-Toledo).

To carry out these analyses, a small amount of the sample, about 10 mg, was introduced into a suitable aluminium capsule, which was hermetically sealed under pressure crucible and placed inside the instrument with the reference sample, an empty capsule (Figure 61).

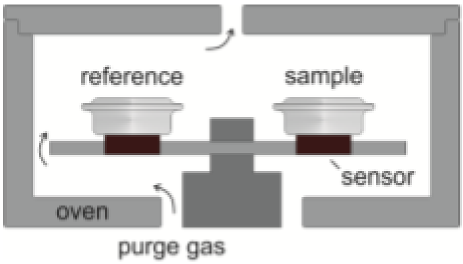


*Figure 61. Setup of a DSC measure.*

During the analysis both crucibles were subjected to the same heat ramp, as the temperature obtained from the two crucibles was different as the reference crucible was empty.

The heat ramp consisted of three cycles with the same heating and cooling rate of 20°C/min and under inert atmosphere (N2): first it was heated from 25°C to 200°C, then cooled again to 25°C and finally heated again to 200°C to obtain the transition temperature.

After performing the differential scanning calorimetry, the data acquisition program displays the data represented in a diagram showing the enthalpy variations that occur in the temperature range of the thermal cycle established for the previously entered thermal program. Therefore, the instrument recorded the difference in temperature and the heat absorbed, which allowed the detection of different thermal transitions in the sample, such as the glass transition (Tg), thermal evaporation, crystallization and melting, which are represented as exothermic or endothermic peaks in a DSC thermograph.

In particular, the glass transition temperature is shown as an endothermic sigmoid change of the baseline. Three different temperature values were evaluated: Tg start corresponding to the sigmoid starting point, Tg inflection corresponding to the tipping point and Tg midpoint which is the mean temperature between the start point and the end point of the sigmoid curve.

### 3.11.2. UV-DSC

The DSC, together with UV light can be used effectively to study the UV curing reaction. It can be used to study curing time, curing enthalpy, light source effect (wavelength, intensity), photoinitiator concentration, curing temperature and purge gas (nitrogen or oxygen).

The instrumental setup is basically equivalent to that of a regular heat flux DSC, except for the two light guides that are mounted into the lid of the measuring cell as shown in Figure 62.

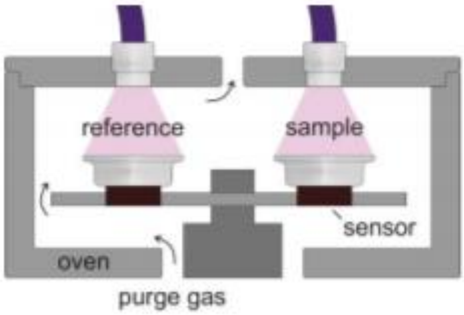


Figure 62. Setup of a UV-DSC measure.

### 3.11.3. Contact angle

With the contact angle measurement technique, surface tension values of solid samples have been obtained.

The contact angle is the angle formed in the contact zone of a drop with the surface. so that it extends exhibiting a certain angle.

The geometric magnitude is defined as the angle formed by the solid-liquid and liquid-vapor interfaces at any point of the line of intersection of the solid-liquid-vapor system interfaces as shown in the Figure 63.[69]

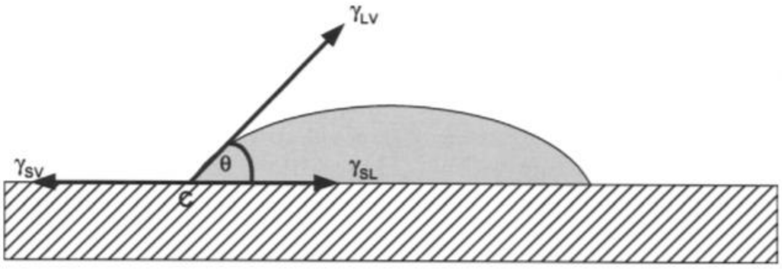


Figure 63. Contact angle of a liquid droplet deposited in the surface of a solid. Representation of the thermodynamic equilibrium at the triple point C.

In our case it would be the example of a contact angle of a liquid in contact with a solid. In this way, when the drop of the liquid used, such as water, wets the surface of our sample, extending over it, a solid-liquid interface is created that replaces the solid-liquid-vapor interface that was found at the beginning.

If the drop of water on the surface is attracted by the solid surface, it will be completely extended so that the contact angle will be 0º and therefore it is a hydrophilic surface. A greater contact angle will mean a lower hydrophilic force on the surface. When the value of the contact angle exceeds 90° it will be hydrophobic (Figure 64)[15].

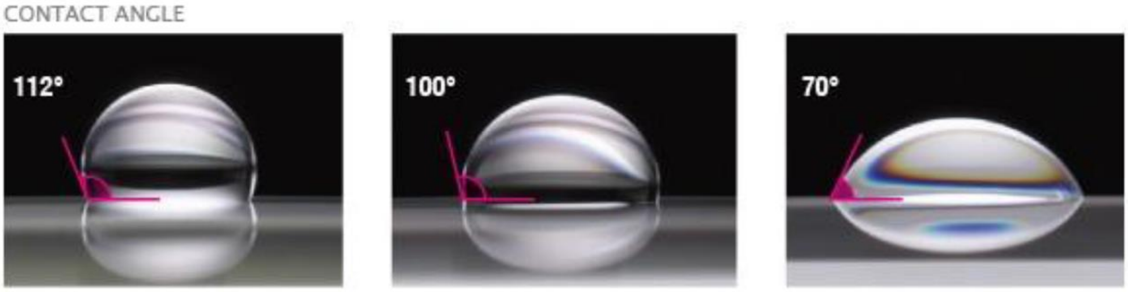


*Figure 64. Drops on surfaces with different surface energy, from lower to higher, assuming the same liquid.*

The optical contact angle was analysed using an OCA 20 instruments (Dataphysics Co., Germany), as shown in Figure 65.

*Figure 65. OCA 20 instruments (Dataphysics Co., Germany) used for contact angle measurements.*

This equipment used to measure surface tension through the contact angle is composed of the following elements:

- Syringe, which allows a drop of the chosen liquid to be deposited with total precision thanks to the controls that modify the position of our sample and the syringe and the regulating system.
- Thermostatic chamber. This is a glass or quartz chamber with an opening at the top where the syringe needle is located.
- CCD camera.  It consists of an eyepiece with a digital video camera reproducing the image received from the camera on the computer.
- Light source. It optimizes the image of the drop, distinguishing more clearly the shapes of the image, increasing or decreasing the intensity of the light.
- Software. Software that analyses the drop and obtains objective results.

### 3.11.4. Tensile test

The tensile test is a fundamental destructive testing process of material science and engineering in which a sample is subjected to controlled stress until failure. The properties that are directly measured by a tensile test are tensile strength, breaking strength, maximum elongation and area reduction. From these measurements the following properties can also be determined: Young's modulus, Poisson ratio, yield strength and strain-hardening characteristics.

To determine the mechanical properties of our material, the uniaxial stress analysis was performed.

In this type of testing, alignment is critical for composite testing applications because composites are anisotropic and generally brittle, as anisotropy means that the properties and strength of the material differ depending on the direction of the force or load applied.

Thus, the tensile strength of a composite material is very high in the direction parallel to the orientation of the fibre, while the tensile strength is much lower if tested in any other direction. To determine the maximum tensile strength in the direction parallel to the fibre direction, the tensile test must have superior axialload-string alignment.

All the samples were tested by using a dynamometer Zwick/Roell BT-FR010TH.A50 with a 10 kN load cell shown in Figure 66.

*Figure 66. Zwick/Roell BT-FR010TH.A50 with a 10 kN load cell.*

In the Figure 67 we can see how our specimen would be placed in the tensile test.

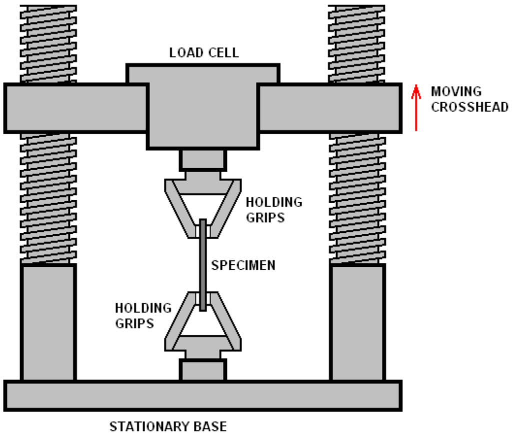


*Figure 67. Tensile testing of composite.*

The specimen used in the tensile test had a rectangular shape that was cut from a compression moulded sample using a circular saw Figure 68.

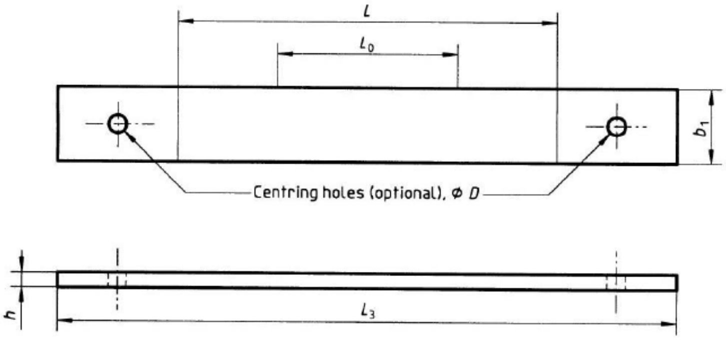


*Figure 68. Specimen used in the tensile test (shape and dimension).*

The operative parameters, as the elongation speed set at 0.8 mm/min and the dimensions of the specimen were scaled from the international standard used for shown in Table 2 (ISO 527-4):

| PROPERTY | DIMENSION (MM) |
|---|---|
| OVERALL LENGTH ($L_3$) | ≥250 |
| DISTANCE BETWEEN END TABS ($L_2$) | / |
| WIDTH ($b_1$) | 25 ± 0.5 or 50 ± 0.5 |
| THICKNESS ($H$) | 2÷10 |
| GAUGE LENGTH ($L_0$) | 50 ± 1 |
| INITIAL DISTANCE BETWEEN GRIPS ($L$) | 150 ± 1 |

*Table 2. Data from the international standard used for testing isotropic and orthotropic fibre-reinforced plastic compounds.*

### 3.11.5. Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) is an electron microscopy technique capable of producing high-resolution images of the surface of a sample using electron-matter interactions. It uses a beam of electrons instead of a beam of light to form an image.

Scanning Electron Microscopy (SEM) was used to analyse the fracture of the surface of the composite sample and identify the causes of the failure.

From the signals derived from the electron-sample interactions it is possible to obtain information about the sample such as its external morphology (texture), the chemical composition and crystal structure and the orientation of the materials that make up the sample. In most applications, data is collected over a selected area of the sample surface and a two-dimensional image is generated showing spatial variations in these properties.

The SEM is also capable of performing location analysis of selected points in the sample; this approach is especially useful in the qualitative or semi-quantitative determination of chemical compositions (using EDS), crystal structure and crystal orientations (using EBSD).

In Figure 69 we can see a general scheme of the Scanning Electron Microscope (SEM) technology.

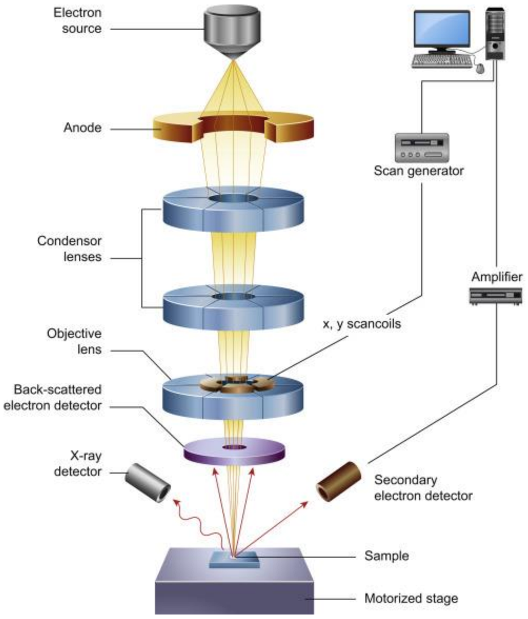


*Figure 69. Scanning Electron Microscope (SEM).*

SEM technology is composed of the following essential elements:

- Source of electrons ("gun")
- Electron lenses
- Sample stage
- Detectors for all signals of interest.

- Display / data output devices
- Infrastructure requirements: Power supply, vacuum system, cooling system, vibration-free floor, room free of environmental magnetic and electric fields.

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on the detectors it accommodates.

The scanning electron microscope used in this project is an EVO 50 Extended Pressure produced by ZEISS and is shown in Figure 70.

*Figure 70. SEM EVO 50 Extended Pressure by ZEISS.*

# 4. RESULTS AND DISCUSSION

The results of the development and characterisation of the glass fibre reinforced polymer composite manufactured from the recycling of waste from the wind industry are presented below.

## 4.1. Samples of the glass fibre reinforced polymer composite

The result of samples prepared with epoxy matrix loaded with 60 wt.% of recycled fibre is shown in the following Figure 71:

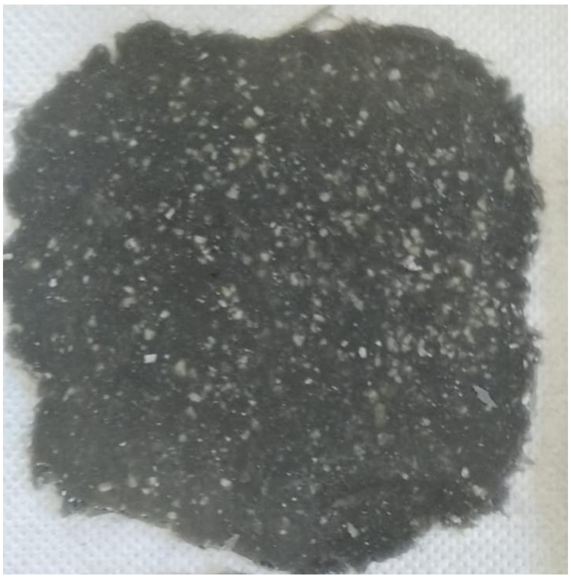


*Figure 71. Sample of glass fibre reinforced polymer composite.*

The thermal and mechanical characteristics of this new composite were studied in previous research and the results obtained are shown in Table 3:

| **THERMAL CHARACTERIZATION** | |
|---|---|
| **Real glass fibre content (%)** | 51 ± 5.90% |
| **$T_g$ (°C)** | 70°C |
| **MECHANICAL CHARACTERIZATION** | |
| **Tensile modulus (GPa)** | 7.49 ± 0.72 |
| **Tensile strength (MPa)** | 35.32 ± 5.17 |
| **Elongation at break (%)** | 0.62 ± 0.21 |

*Table 3. Thermal and mechanical properties of the glass fibre reinforced polymer composite.*

### 4.1.1. Results from OCA

In our case, as we will be based on the study of the surface coating of our new composite material, it is of vital importance the study and characterization of the surface where we will deposit our coating solutions.

In this way we will focus on the wetting of the surface. Knowledge of the wettability phenomenon is of great importance in applications such as the production of composite materials. For this reason, contact angle tests have been carried out using the sessile drop method, monitoring with software equipment coupled to the OCA- equipment.

The drop surface analysis software of the OCA measuring device calculates the contact angle from the images and videos captured during the tests. A representative example of these measurements can be seen in the Figure below:

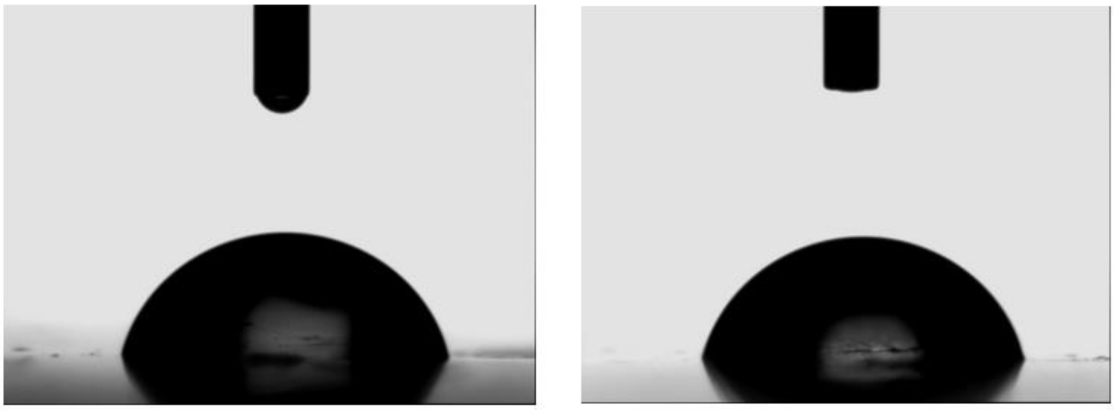


*Figure 72. OCA measurement images: a) PMMA sheets b) Metallic sheets.*

In *Figure 72* we can see the images obtained from the software of the OCA equipment for the two measured samples during contact angle testing: a sample of the composite material manufactured between two metallic sheets and the other manufactured between PMMA. The OCA measurement has been made in both to check if the material used in the mould during the moulding stage affects the final properties of our material.

For the analysis and characterization of the surface of the recycled composite material the contact angle was measured by the OCA technique. Approximately 12 measurements were made on each of the samples obtaining an average value. The results are shown in Table 4:

| | **PMMA** | **METALLIC** |
|---|---|---|
| **CONTACT ANGLE** | 66.59 | 81.91 |
| **AVERAGE VALUE** | 74.25 | |

*Table 4. Average values from OCA technique.*

The results for both samples differ, although not to a great extent. These differences may be due to the roughness of the different samples. As we already know, the contact angle is closely related to the wettability of the system. This in turn is influenced by various factors such as the roughness of the system. The higher the surface roughness, the lower the contact angle.

Therefore, we can say that the difference in results between both samples may be due to the fact that the moulds used during the moulding stage in the sintering of the recycled composite material had small scratches that would damage the surface of the composite material sample.

Another factor that may have affected is the porosity of the sample. In the case of samples with not totally uniform surfaces, the measured angle of a specific drop on the surface of the material may have been when it rested on one of the pores of the material.

As we have seen previously, the results of the contact angle measurement show a contact angle of around 74.25 degrees which indicates a low wettability. In addition, the contact angle is also related to the surface tension. A system with a low dihedral angle, has low solid-liquid interfacial energy and promotes liquid penetration along the solid-solid contacts. For this reason, one of the prospects for the future is to increase the characterization of the surface of the material with the analysis of the surface tension.

Furthermore, in the results obtained from the coating of recycled material that appear later in the section 4.3, we can see that the poor results obtained are related to the low wettability of the material.

## 4.2. Coating solutions results

As detailed above, a scanning calorimetry with UV has been performed on each of the solution samples to determine the photo reactivity of the solutions before they are exposed to the UV lamp. Then to evaluate if the sample has been totally cross-linked the DSC has been performed in addition to obtaining the glass transition temperature, as well as to observe if any other thermal event occurs at a certain temperature.

### 4.2.1. UV-DSC results

The operating conditions chosen were at 30% of potential of the lamp and 5 minutes during the UV-DSC measurement.

#### *4.2.1.1. Solution of AralditeBY158 and Omnicat440*

For the solution of AralditeBY158 and Omnicat440, the UV-DSC measurement was done for both concentrations of Omnicat440. An example of the type and shape of the graph obtained from the UV-DSC is shown in Figure 73.

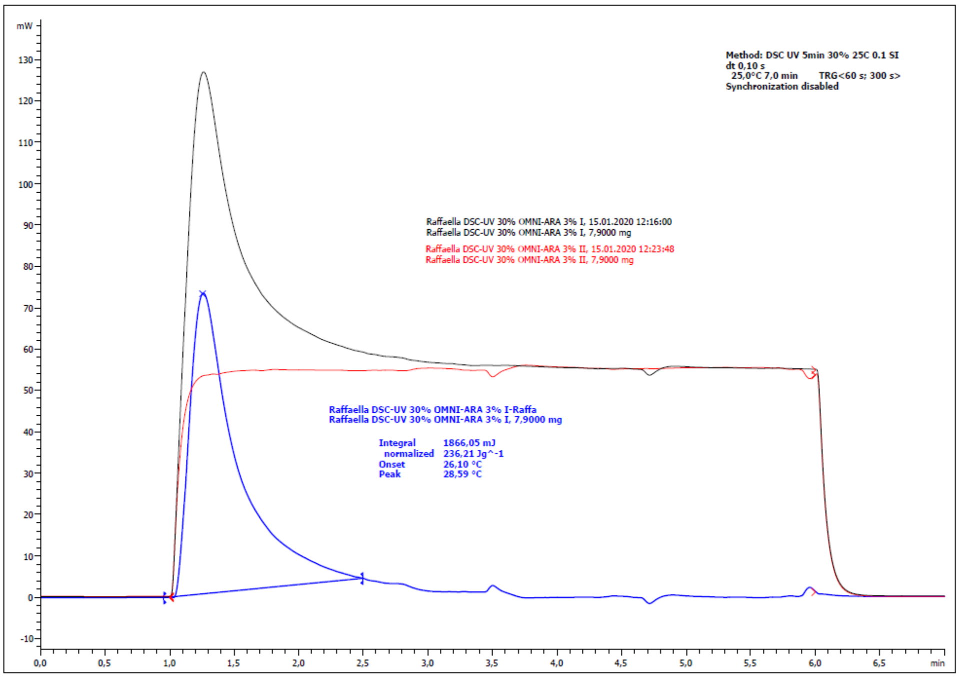


*Figure 73. UV-DSC curve from software equipment of solution of AralditeBY158 and Omnicat440 (3%).*

From the UV-DSC technique, a peak is obtained whose characteristic data that is necessary for the study of coating solutions is the value of the integral normalized measured in J/g as shown in Figure 74.

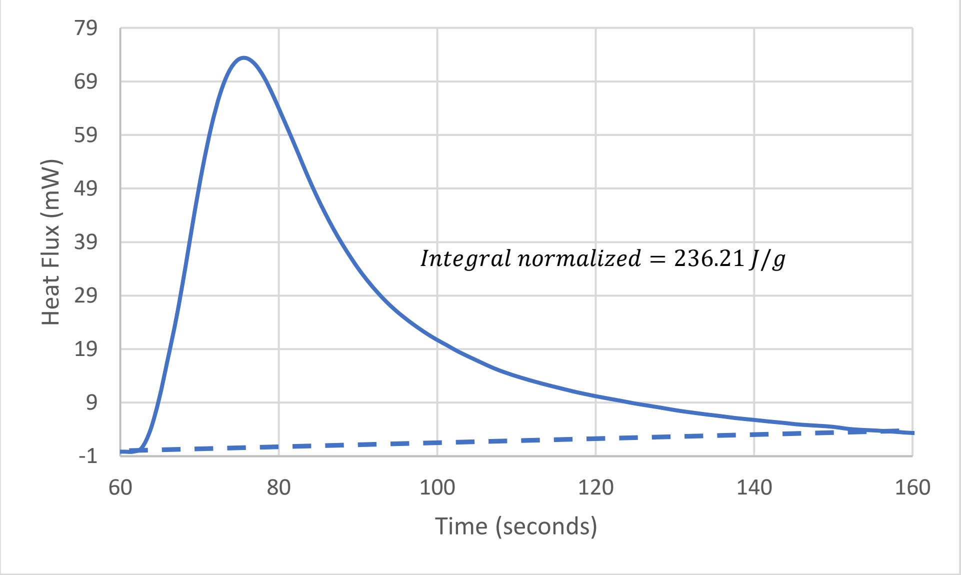


*Figure 74. UV-DSC curve of solution of AralditeBY158 and Omnicat440 (3%).*

For the solution at 3% of Omnicat440, the integral normalized obtained is equal to 236.21 J/g.

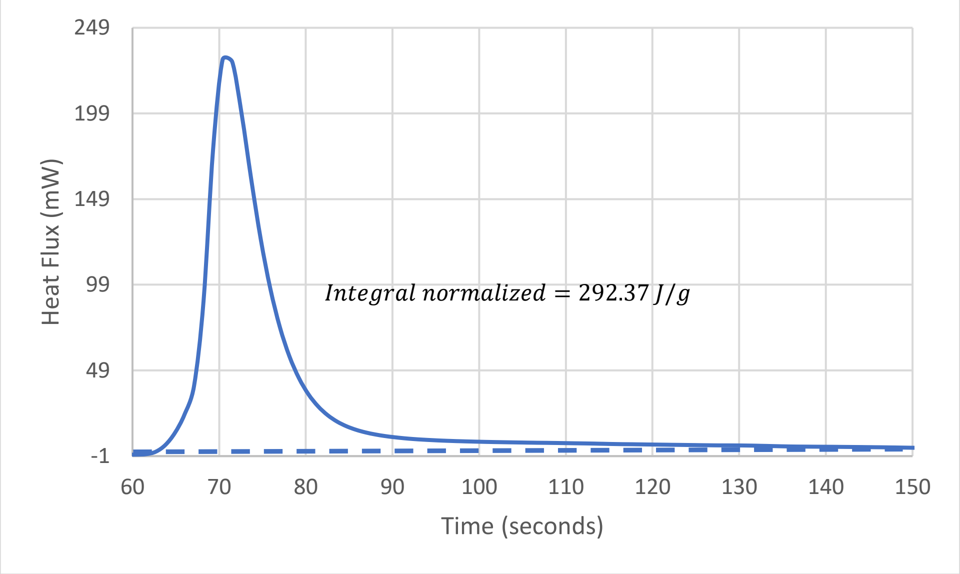


*Figure 75. UV-DSC curve of solution of AralditeBY158 and Omnicat440 (5%).*

In Figure 75 the integral normalized obtained for the solution at 5% of Omnicat440 was equal to 292.37 J/g.

#### *4.2.1.2. Solution of AralditeBY158, Aradur21 and Omnicat440*

This solution solidified after 30 minutes. Its viscosity increases rapidly. Therefore, it could not be characterized. The solution had to be prepared again and immediately characterized.

UV-DSC had been performed. However, no cross-linking had occurred as shown in Figure 76.

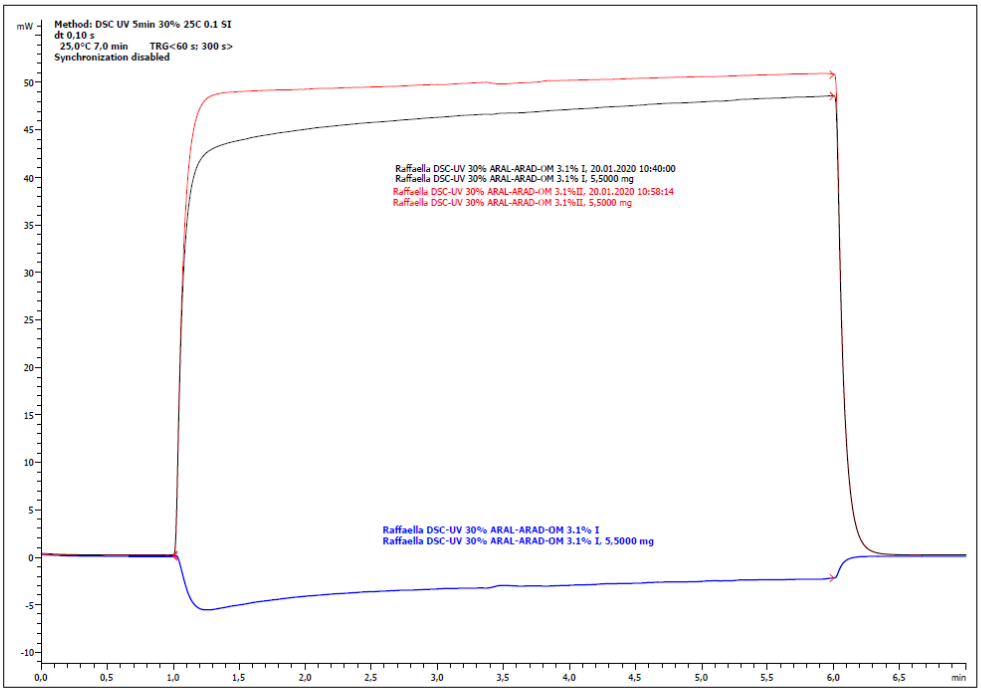


*Figure 76. UV-DSC curve from software equipment of solution of AralditeBY158, Aradur21 and Omnicat440.*

#### *4.2.1.3. Solution AralditeBY158, Succinic Anhydride and Omnicat440*

As a consequence of the above results with the curing agent Aradur21, another curing agent was used at different percentages of Omnicat440. In this case, Succinic Anhydride was chosen because of Aradur21 possibly inactivated the AralditeBY158.

However, problems during the mixing of the solution occurred. The result was a transparent solution with white particles (Figure 77). Therefore, it was decided to heat the solutions in an oil bath to 40-50 degrees.

*Figure 77. Result of mixing solution of AralditeBY158, Succinic Anhydride and Omnicat440 (3%).*

Finally, a homogeneous solution was achieved, but after a certain time the mixture is no longer homogeneous, and a whitish part appears. Therefore, this solution was ruled out.

#### *4.2.1.4. Solution of AralditeBY158, Phthalic Anhydride and Omnicat440*

As a consequence of the bad results using the Succinic Anhydride, it was replaced by another anhydride, the Phthalic Anhydride. The UV-DSC had been performed for both concentrations of Omnicat440. The results are shown in the following Figures 78 and 79:

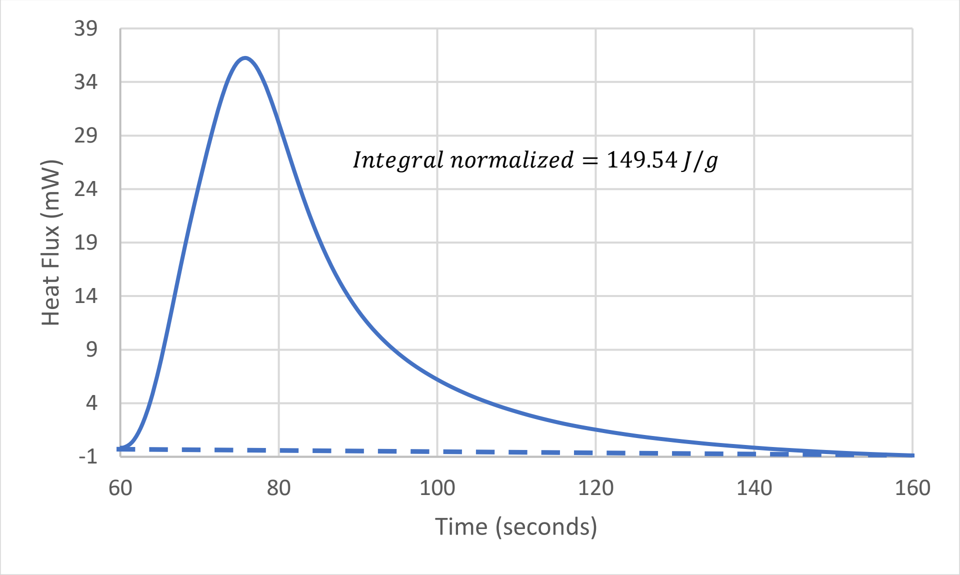


*Figure 78. UV-DSC curve of solution of AralditeBY158, Phthalic anhydride and Omnicat440 (3%).*

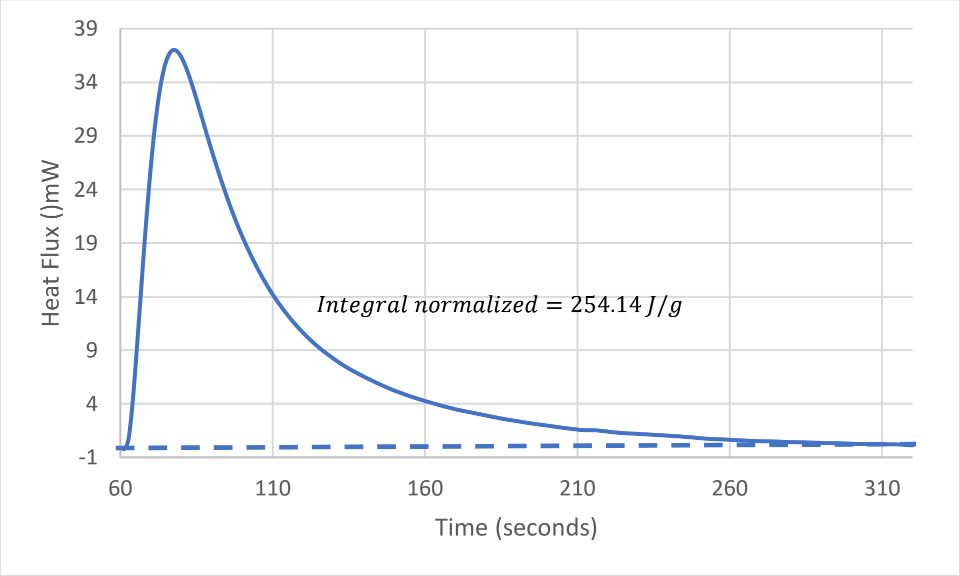


*Figure 79. UV-DSC curve of solution of AralditeBY158, Phthalic anhydride and Omnicat440 (5%).*

Using the curing agent Phthalic Anhydride, the integral normalized values for 3% and 5% were 149.54 J/g and 254.14 J/g respectively.

### 4.2.2. DSC results

After the UV-DSC measurements, DSC equipment was used to obtain from the different coating solutions the glass transition temperature that manifests itself as a step change in the specific heat capacity. For this reason, a range of temperatures is taken into account when calculating the glass transition temperature, in addition to the fact that it is affected by time-dependent phenomena, such as the rate of heating. Therefore, in order to establish the glass transition temperature as a single numerical value, some explanation is necessary.

Usually, Extrapolated Onset Temperature (Tf) or Midpoint Temperature (Tm) or Inflection Temperature (Ti) is selected to represent the temperature range over which the glass transition takes place as shown in Figure 80.

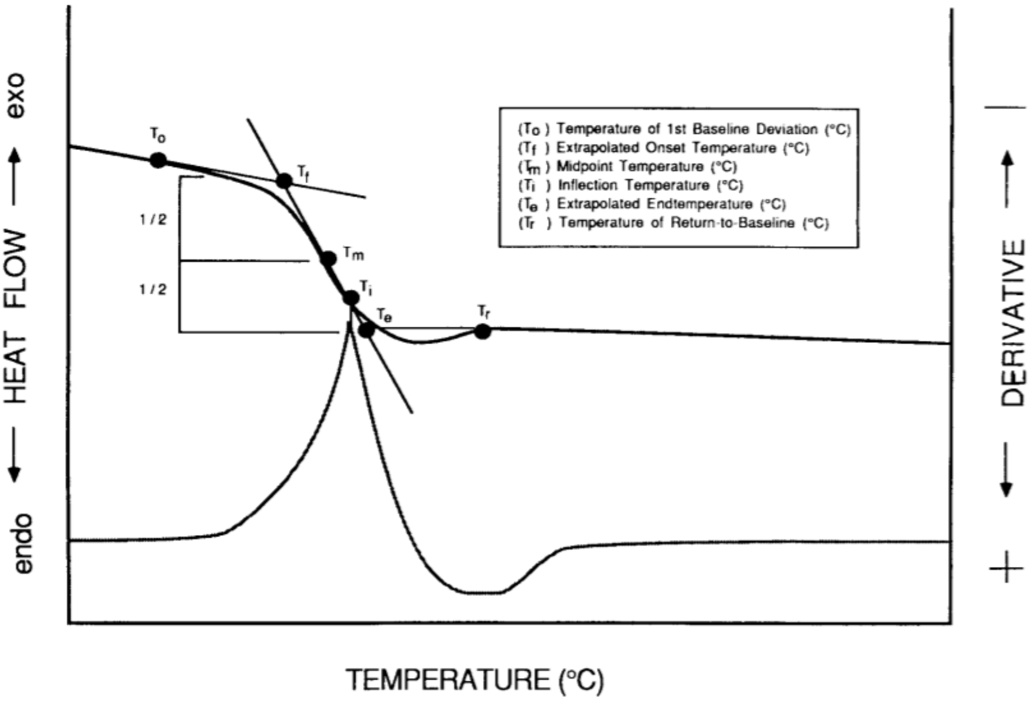


*Figure 80. Glass Transition Region Measured Temperatures.*

In this work the temperature of the Inflection Point has been chosen as Tg. The DSC results from the different coating solutions are presented in the following sections.

#### *4.2.2.1. Solution of AralditeBY158 and Omnicat440*

Two solutions of AralditeBY158 and Omnicat440 were prepared with different concentration of Omnicat440 to study if the concentration of the photoinitiator affects to the result of the finishing surface. The percentages were 3% and 5%.

Firstly, a solution with 3% of Omnicat440 was prepared and measured with the DSC. The DSC was performed on sample with the following thermal cycle: from 25ºC to 250ºC, 250ºC to 25ºC and finally from 25ºC to 250ºC with a speed of 20ºC/min. The results were rare values, strange residual peaks appear which tell us that the sample after the exposure of the UV light is still active. Moreover, after the thermal cycle, we opened the sample, which was changed to brown colour, it had deteriorated.

Therefore, to avoid its deterioration, another thermal cycle with a maximum temperature of 200ºC (Figure 81) was carried out.

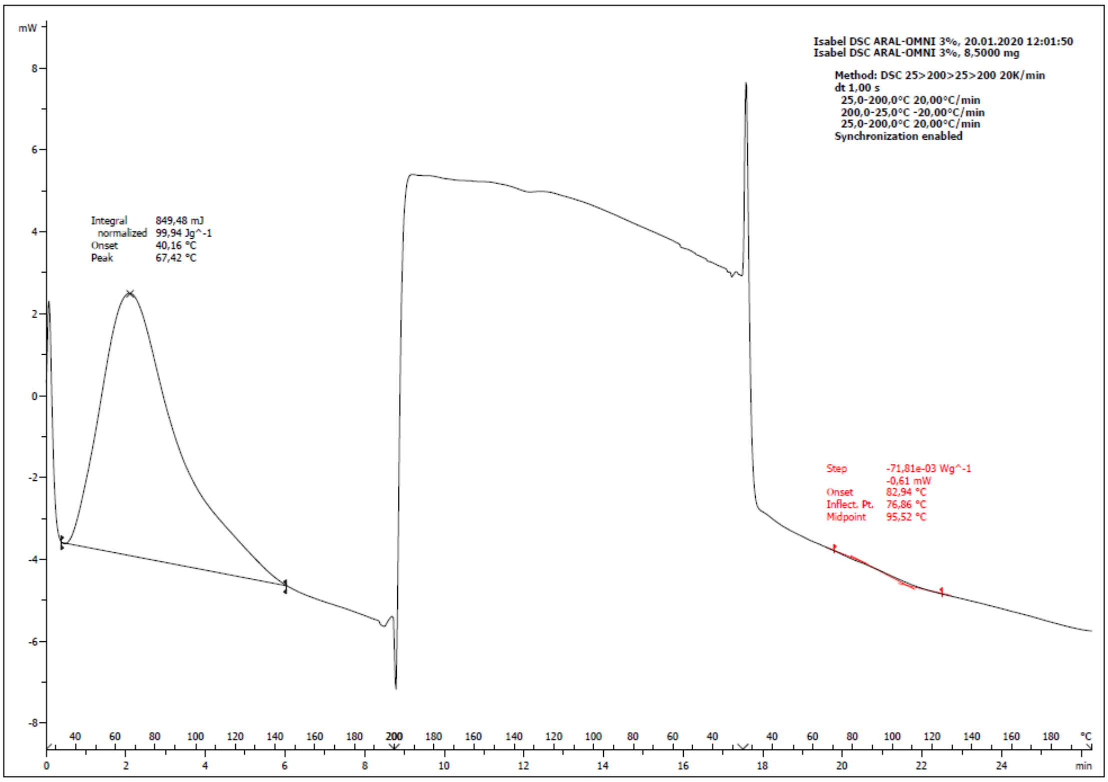


*Figure 81. DSC curve from software equipment of solution of AralditeBY158 and Omnicat440 (3%).*

In this case, using the maximum temperature condition during the thermal cycle equal to 200ºC the results obtained were better.

From this result, it was to be expected that solution without a cross-linking agent would be less efficient in the cross-linking of the solution. In this way, the epoxy compound AralditeBY158 together with the photoinitiator Omnicat440 form positively charged macro-radicals which form oxydriles at each stage of the reaction. These oxydriles can react with the epoxide.

Thanks to this result we can affirm that to obtain an efficient reticulation of the solution under UV light it is necessary to use a reticulating agent. For this reason, after the measurement of the UV-DSC, a DSC measurement is necessary to carry out to verify if the reticulation was 100% through the visualization or not of a residual peak in the first stage of heating which is used to understand the reactivity of the resin.

The values of the different temperatures from the peak appears in the first stage of heating are observed better in Figure 82.

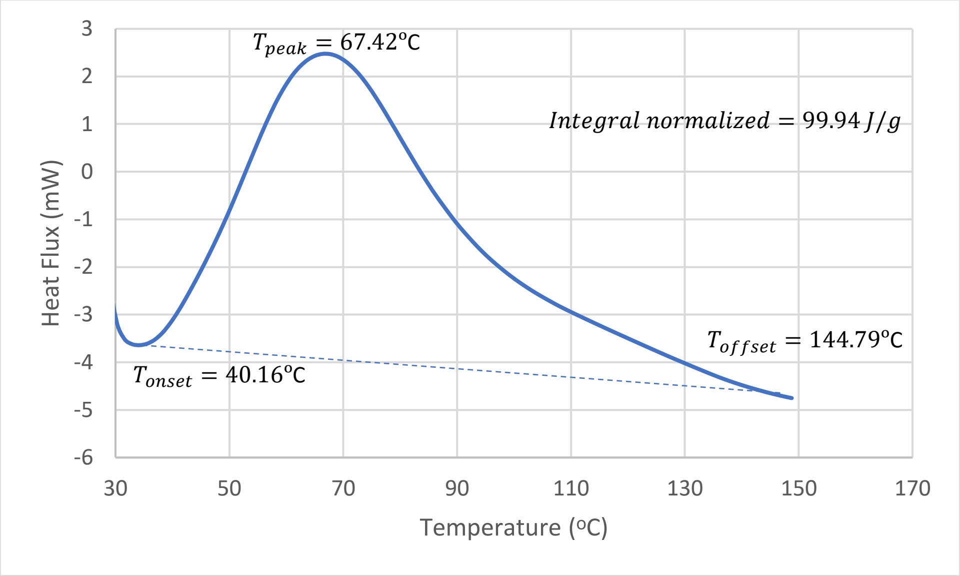


*Figure 82. DSC curve from the first phase of the thermal cycle of solution of AralditeBY158 and Omnicat440 (3%).*

This first peak that appears has an integral normalized value of 99.94 J/g

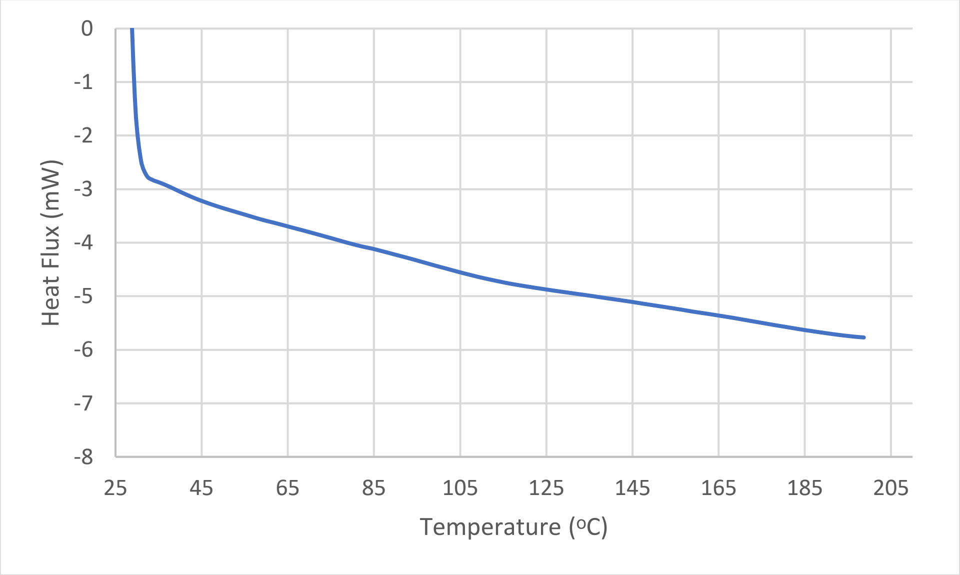


*Figure 83. DSC curve from the second phase of solution of AralditeBY158 and Omnicat440 (3%).*

In Figure 83, from the second phase of the thermal cycle we can observe the glass transition temperature of our sample after the reticulation process firstly under the UV lamp and then with the DSC until the reticulation of the solution is completed obtaining the Tg which is represented with the Inflection point because is the point of inflection of the curve and therefore more corresponding to the definition of Tg. The value obtained is equal to 76.86ºC.

However, the first peak should not appear. This suggests that not all the sample has been cured correctly and therefore remains active. For this reason, it was decided to subject the sample to a heat treatment for 1 and 2 hours at 100ºC after the UV curing process in order to achieve the disappearance of the peak. The results are shown in Figure 84.

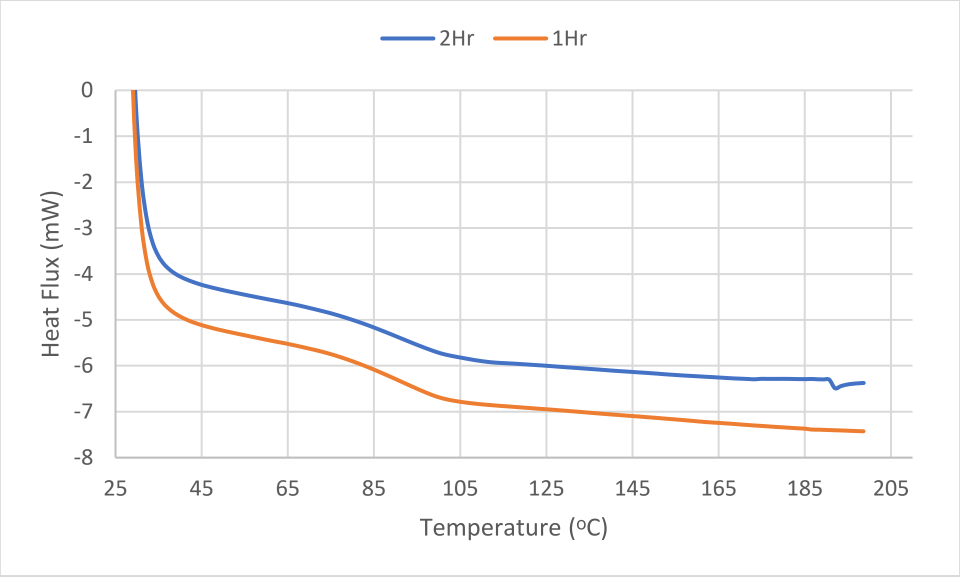


*Figure 84. DSC curve of solution of AralditeBY158 and Omnicat440 (3%) after 1 and 2 hours of thermal cure in oven.*

In both graphics, the first peak has disappeared indicating that the sample has totally reticulated. For the solution of Omnicat440 (3%) the Tg values are 92.09ºC and 90.46ºC after 1 and 2 hours respectively.

Therefore, from the data it is concluded that the thermal pre-treatment eliminates the peak corresponding to the reactivity of the epoxy resin in the first part of the thermal cycle. Furthermore, 1 hour of thermal pre-treatment at 100 ºC would be enough to complete the reticulation of the resin. The values do not differ much from 2 hour of thermal pre-treatment.

Moreover, the solution with the 5% of Omnicat440 was also measured. The results appear in the following Figure 85 and 86.

In the first part of the thermal cycle, a peak is also observed as in the solution with the 3% of Omnicat440.

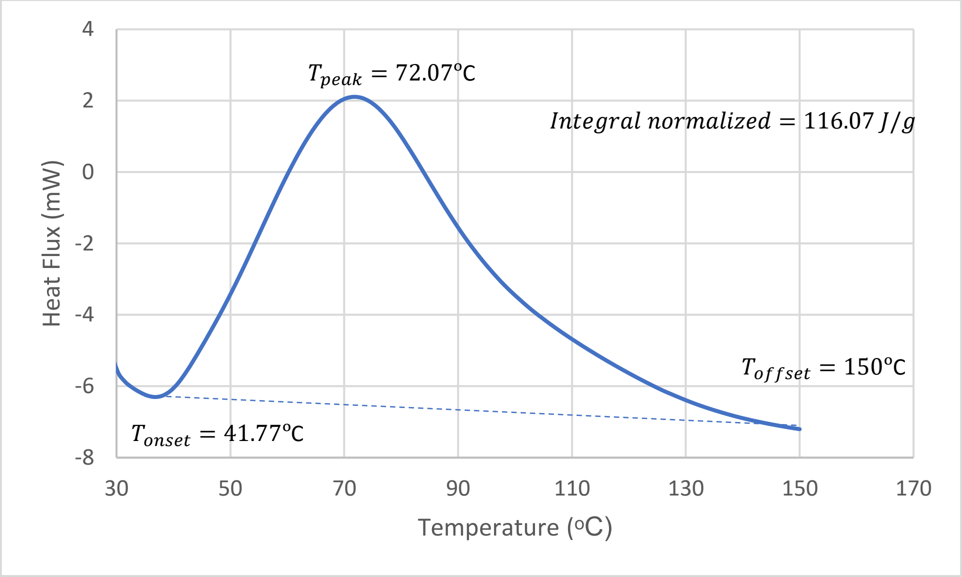


*Figure 85. DSC curve from the first phase of the thermal cycle of solution of AralditeBY158 and Omnicat440 (5%).*

Using a higher percentage of Omnicat440, the value of the integral normalized from the peak increases. For the 5% of Omnicat440 the integral normalized obtained is 116.07 J/g and for the 3% this value is equal to 99.94 J/g.

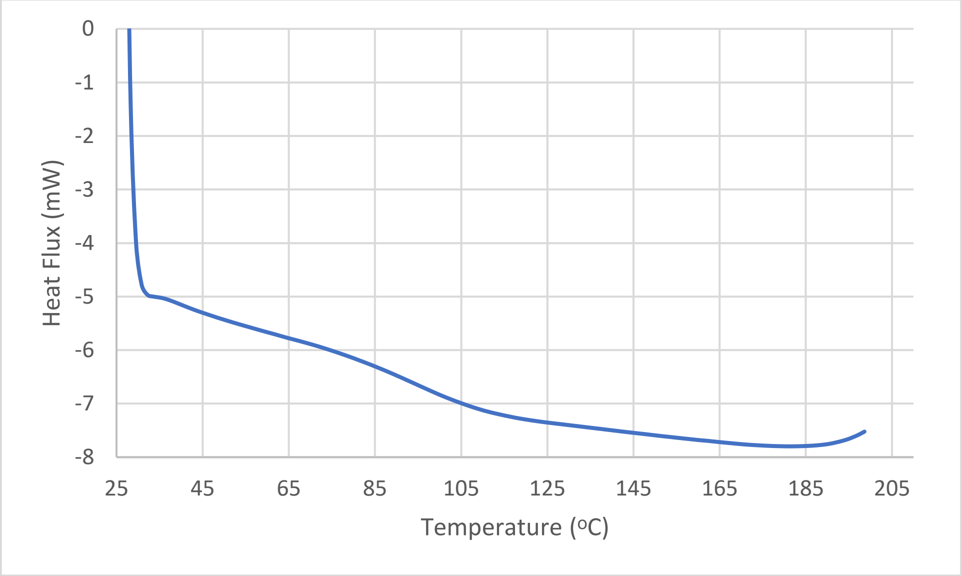


*Figure 86. DSC curve from the second phase of the thermal cycle of solution of AralditeBY158 and Omnicat440 (5%).*

In the second part of the thermal cycle, as shown in Figure 86, the glass transition temperature is obtained and equal to 95.08°C.

As a consequence of the similar results to the solution with the 3% of Omnicat440, the method used was the same. The sample was also subjected to a thermal treatment before the DSC measurement. The results are shown in the following Figure 87.

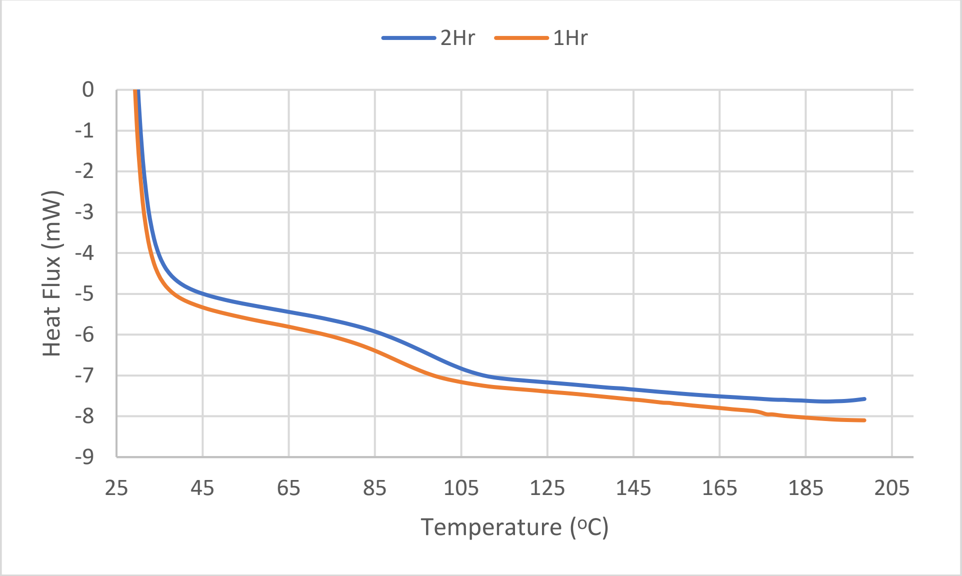


*Figure 87. DSC curve of solution of AralditeBY158 and Omnicat440 (5%) after 1 and 2 hours of thermal cure in oven.*

For the solution of AralditeBY158 and Omnicat440 (5%) the Tg values are 89.42°C and 98.08°C after 1 and 2 hours respectively. In this case, unlike the 3% Omnicat440 solution, Tg results are better the longer the thermal pre-treatment time for the 5% of Omnicat440.

#### *4.2.2.2. Solution of AralditeBY158, Aradur21 and Omnicat440*

The DSC results from the new solution with the curing agent Aradur21 and 3% of Omnicat440 under the same conditions of thermal cycle are shown in the following Figure 88.

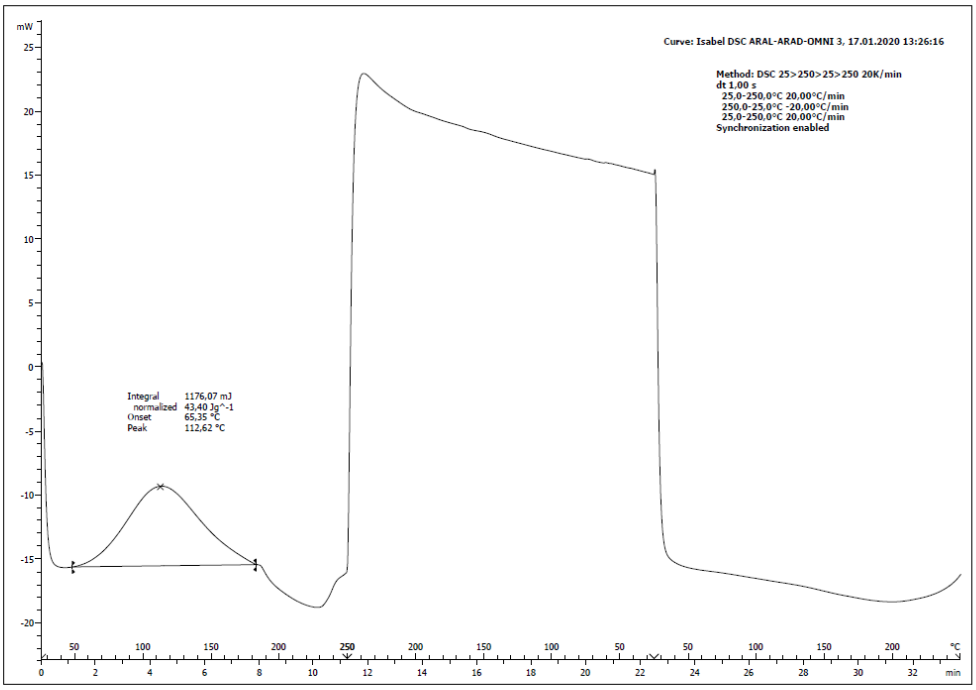


*Figure 88. DSC curve from software equipment of solution of AralditeBY158, Aradur21 and Omnicat440 (3%)*

For this sample the Tg value is not obtained because in this case, as we said before after the UV-DSC result, the cross-linking is not produced due to the presence of the amine cross-linking agent that inhibits the polymerization of the epoxy cation.

#### *4.2.2.3. Solution AralditeBY158, Phthalic Anhydride and Omnicat440*

To achieve a better mixing solution, the Succinic Anhydride was replaced by another anhydride called Phthalic Anhydride. The analytical result of the DSC for both concentrations of Omnicat440 are shown in Figures 89 and 90.

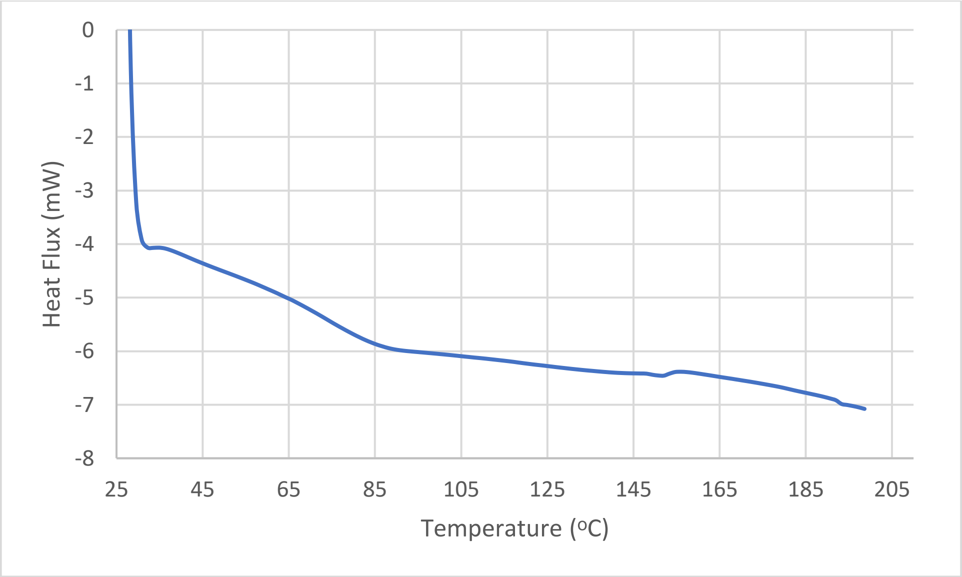


*Figure 89. DSC curve of solution of AralditeBY158, Phthalic anhydride and Omnicat440 (3%).*

For the solution of AralditeBY158, Phthalic Anhydride and Omnicat440 (3%) the Tg values is 74.14ºC.

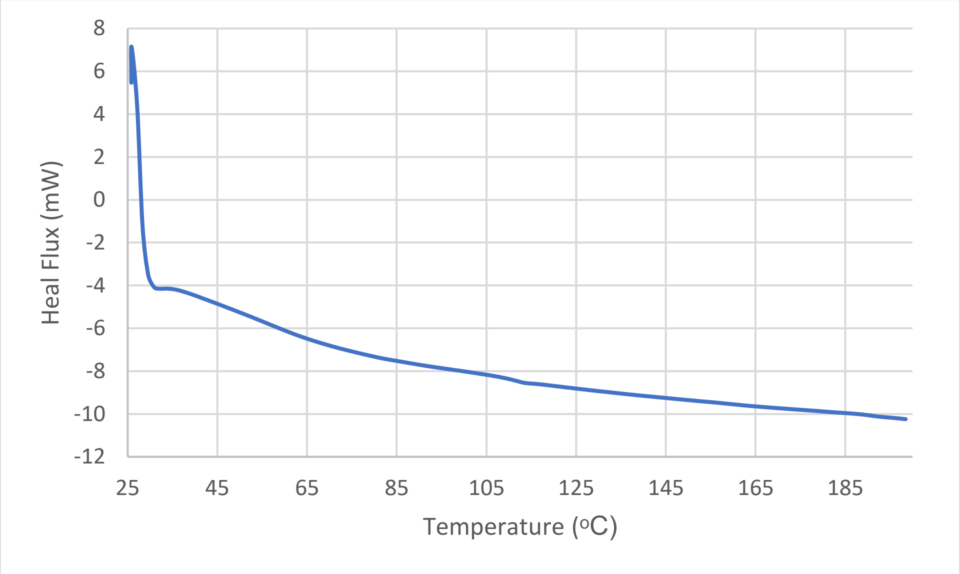


*Figure 90. DSC curve of solution of AralditeBY158, Phthalic anhydride and Omnicat440 (5%).*

In Figure 90, the DSC results for the solution of AralditeBY158, Phthalic anhydride and Omnicat440 (5%) show us that there are two values of Tg, therefore a hypothesis would be that by increasing the amount of the photoinitiator in this case from 3% to 5% for the same amount of anhydride two phases are formed, one due to the cationic polymerization of the epoxy by UV radiation and the other due to the condensation of the anhydride with the hydroxyl.

Another hypothesis would be that there is some immiscibility in the sample as sometimes the glass transition temperature can be used to assess the miscibility of amorphous mixtures or polymer mixtures. Therefore, when two amorphous materials are miscible, a Tg will normally be observed on the DSC curve, while when the samples are immiscible, two Tg values will normally be observed. So perhaps above a certain amount of Omnicat440, in this case 5%, there is some immiscibility of the solution.

Consequently, to obtain more information about the process involved it would be useful to perform a Dynamic Mechanical Analysis (DMA) since it can recognize small transition regions that are beyond the resolution of DSC.

In any case, it should also be taken into account that the anhydride reacts with heat and not with UV light, so the appearance of two Tg values could also be because the 5% of photoinitiator reacts firstly with UV light with the epoxy resin and then with the anhydride during heating.

### 4.2.3. Summary results obtained from UV-DSC and DSC coating solutions.

After carrying out the UV-DSC measurements of the different coating solutions, we have focused on the value of the integral normalized measured in J/g to realize the analysis and comparison between the different samples. This value relates to the reticulation power presented by the sample. In this way, the greater the value of the integral normalized, the greater the reticulation and therefore it will be more resistant to UV light.

A summary of the values of the integral normalized obtained in the coating solutions are presented in Table

| COATING SOLUTION | Integral Normalized (J/g) |
|---|---|
| **AralditeBY158-Omnicat440 (3%)** | 236.21 |
| **AralditeBY158-Omnicat440 (5%)** | 292.37 |
| **AralditeBY158-Aradur21-Omnicat440 (3%)** | ERROR |
| **AralditeBY158-Aradur21-Omnicat440 (5%)** | ERROR |
| **AralditeBY158-Phthalic anhydride-Omnicat440 (3%)** | 149.54 |
| **AralditeBY158-Phthalic anhydride-Omnicat440 (5%)** | 254.14 |

*Table 5. Values obtained from UV-DSC analyses of coating solutions.*

The values show that the concentration of Omnicat440 used affects the value of the integral normalized. The greater the concentration of Omnicat440, the greater the integral normalized value and therefore the reticulation.

On the other hand, after the DSC measures, the value that interests to analyse is the Tg since the greater this one is, better resistance will have the coating applied to our remanufactured material.

The values of the glass transition temperature obtained from the different coating solutions are presented in Table

| COATING SOLUTION | Tg ($^oC$) |
|---|---|
| **AralditeBY158-Omnicat440 (3%)** | 76.86 |
| **AralditeBY158-Omnicat440 (3%) 1hr** | 92.09 |
| **AralditeBY158-Omnicat440 (3%) 2hr** | 90.46 |
| **AralditeBY158-Omnicat440 (5%)** | 95.08 |
| **AralditeBY158-Omnicat440 (5%) 1hr** | 89.42 |
| **AralditeBY158-Omnicat440 (5%) 2hr** | 98.08 |
| **AralditeBY158-Aradur21-Omnicat440** | ERROR |
| **AralditeBY158-Succinic anhydride-Omnicat440** | ERROR |
| **AralditeBY158-Phthalic anhydride-Omnicat440 (3%)** | 74.14 |
| **AralditeBY158-Phthalic anhydride-Omnicat440 (5%)** | Two values:<br>55.81<br>111.65 |

*Table 6. Values obtained from DSC analyses of coating solutions.*

For the solution of AralditeBY158 and Omnicat440, as in the results of the UV-DSC, the Tg increases with the concentration of Omnicat440. For the 3% the Tg is equal to 76.86ºC while for the 5% it is equal to 95.08ºC.

Moreover, the increase in Tg after stove hours for the same solution may be due to an increase in cross-linking after the curing in the stove because the epoxy can react with the hydroxide groups generated during the cationic polymerization of the epoxy by radiation.

However, the Tg value for the 5% after 1hr is a little bit out of this trend and could be a figure distorted by something else, but considering the result for the 5% after 2hr is higher than the 0hr.

Respect to the time of the thermal pre-treatment, with a concentration of 3% there is almost no difference in the Tg but, it is not the same when we increase the concentration of the photoinitiator, Tg results are better the longer the thermal pre-treatment time.

As we have commented before, for the coating solution formed by AralditeBY158-Phthalic anhydride-Omnicat440, when the concentration of the photoinitiator is increased from 3% to 5%, two Tg values appear which may be due to different possible hypotheses: on the one hand due to the presence of certain immiscibility of the solution and on the other hand due to the amount of the photoinitiator for the same quantity of anhydride.

In this last hypothesis, two phases are formed, one as a result of the cationic polymerization of the epoxy by UV radiation and the other in consequence of the condensation of the anhydride with the hydroxyl.

## 4.3. Remanufactured compound coating results

During the characterization of the coating solutions, each solution has been tested on our remanufactured material. The results obtained are shown below.

### 4.3.1. Solution of AralditeBY158 and Omnicat400.

Firstly, two layers of solution AralditeBY158 and Omnicat440 (3%) were applied to the three glass samples with the help of a brush. Finally, they have been exposed under the UVB lamp for 10 minutes.

In order to check if the bad results obtained are due to the material of the glass samples, it was decided to carry out the coating on the surface of our composite in two ways: using a brush and using the primer instrument. The result is shown in Figure 91.

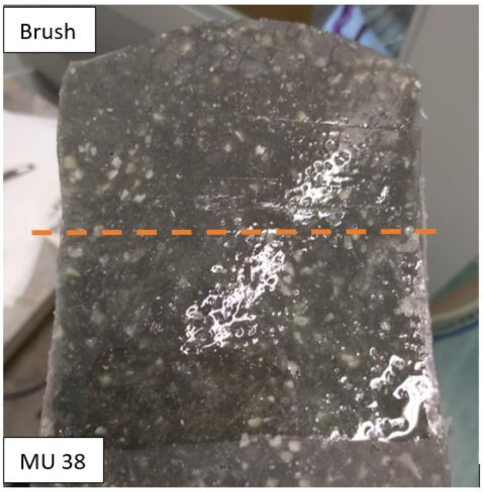


*Figure 91. Results of coating techniques with solution prepared on the surface of sample.*

The result shows that the brush coating technique was bad; the surface coating is not smooth. The same occurs with the square instrument of primer application.

### 4.3.2. Solution of AralditeBY158, Aradur21 and Omnicat440.

As with solution of AralditeBY158 and Omnicat400 (3%), a layer of the solution AralditeBY158, Aradur21 and Omnicat440 (3%) which is more viscous than previous one, has been applied to the glass samples with the help of the brush. The glass samples were left at room temperature for two days. After this time, we can see that the cross-linking has not been carried out completely. Therefore, the glass samples are placed in the oven at Tº= 100°C for 1 hour (Figure 92).

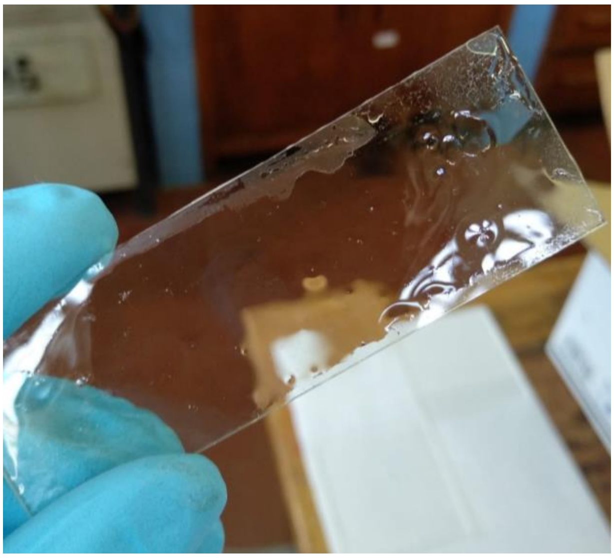


Figure 92. Result of glass sample with a layer of AralditeBY158, Aradur21 and Omnicat440 (3%) solution.

From Figure 92 the results are still bad, a proper final surface coating is not obtained.

### 4.3.3. Solution of AralditeBY158, Succinic Anhydride and Omnicat440

After measuring the UV-curing reaction with the analytic technique UV-DSC of a small sample of the solution of AralditeBY158, Aradur21 and Omnicat440 at different percentages it was observed that it did not reticulate. Maybe it occurred because Aradur21 inhibited AralditeBY158. For this reason, it was decided to replace Aradur21 with an anhydride. Firstly, succinic anhydride was chosen.

The result of the coating of the sample was bad. The brush technique did not work properly, the film formed on the glass was not uniform. Also, the colour of the coating was a whitish, translucent colour, not transparent as shown in the Figure 93.

Figure 93. Result of coating with a solution of AralditeBY158, Succinic Anhydride and Omnicat440 (3%).

### 4.3.4. Solution of AralditeBY158, Phthalic Anhydride and Omnicat440

Because of the bad results using the succinic anhydride, another anhydride was used. In this case phthalic anhydride was used. Moreover, the brush technique during coating was substituted by an airbrush.

The solution of AralditeBY158, Phthalic Anhydride and Omnicat440 (3%) was applied to the three glass samples with the help of an airbrush with air source. Finally, they have been exposed under the UVB lamp for 10 minutes.

The airbrush technique has been much better than with the brush. The film formed on the glass is more uniform in compared to the brush technique, but it still was not perfect.

Thanks to the improved technique of depositing the coating solution on the surface with the help of the airbrush, the coating was done in the same way on the surface of our composite but using an ozone source to avoid any contamination. The result is shown in Figure 94.

*Figure 94. Airbrush coating composite with the solution of AralditeBY158, Anhydride Phthalic and Omnicat440 (3%).*

However, the result remained poor. The coating is not a uniform layer. The result is a surface with an orange peel effect. Then, it was done again by putting a second layer of the solution, depositing more quantity but the results were again bad (Figure 95).

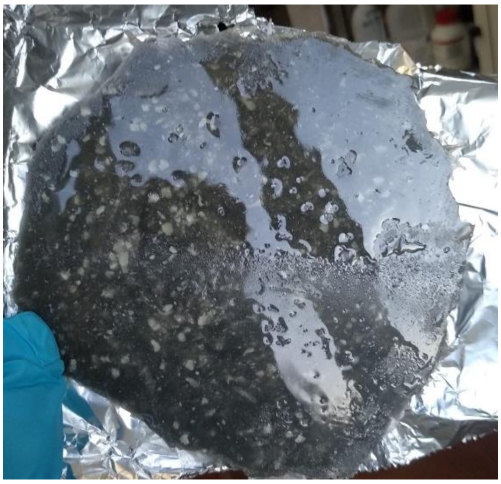


*Figure 95. Airbrush coating composite with 2 layers of the solution of Anhydride Phthalic, AralditeBY158 and Omnicat440 (3%).*

To improve the adhesion of the coating solution to the surface of the composite, a cleaning process with soap and water and isopropanol was carried out before the coating stage. Then was dried with ozone and finally was subjected to a plasma treatment to reduce the hydrophobic character of the surface with the solution Different times of plasma pre-treatment were used (10 and 30 minutes), but there were no differences. The result was the following (Figure 96):

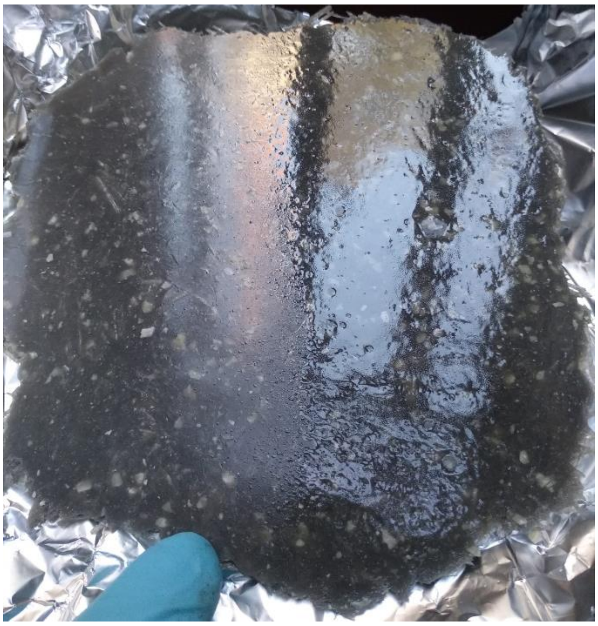


*Figure 96. Airbrush coating composite with the solution of AralditeBY158, Phthalic Anhydride and Omnicat440 (3%) with previous pre-treatment surface.*

In this case, the orange peel effect still appears but to a lesser degree.

To try to get better results, two options were made: one was to make two layers with the airbrush. This way, between the first layer and the second one, the piece was cured under UV light.

The second option was to add a small amount of acetone in the coating solution (10% and 20% of acetone). The best result obtained was this option (Figure 97).

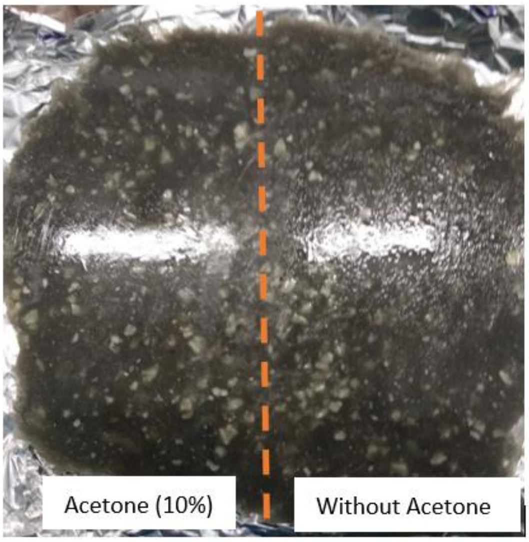


*Figure 97. Airbrush coating composite with the solution of AralditeBY158, Phthalic Anhydride, Omnicat440 (3%) and Acetone (10%) with previous pre-treatment surface.*

However, none of these results are worthwhile.

The same procedure has been carried out with the other solution of AralditeBY158, Phthalic Anhydride and Omnicat440 (5%).

In addition, visually there was no difference between using Omnicat440 (3%) or Omnicat440 (5%).

### 4.3.5. Solution of AralditeBY158 and Aradur21

To find out what the reason is for the poor results during the coating stage, the pre-treatment stage of the composite surface has been tested better. For this purpose, the surface of the composite has been sanded with different sandpapers (400 and 500). Furthermore, the surface has been properly cleaned with soap and isopropanol and treated with plasma for ten minutes. Unfortunately, no improvement happened. The results are shown in Figure 98.

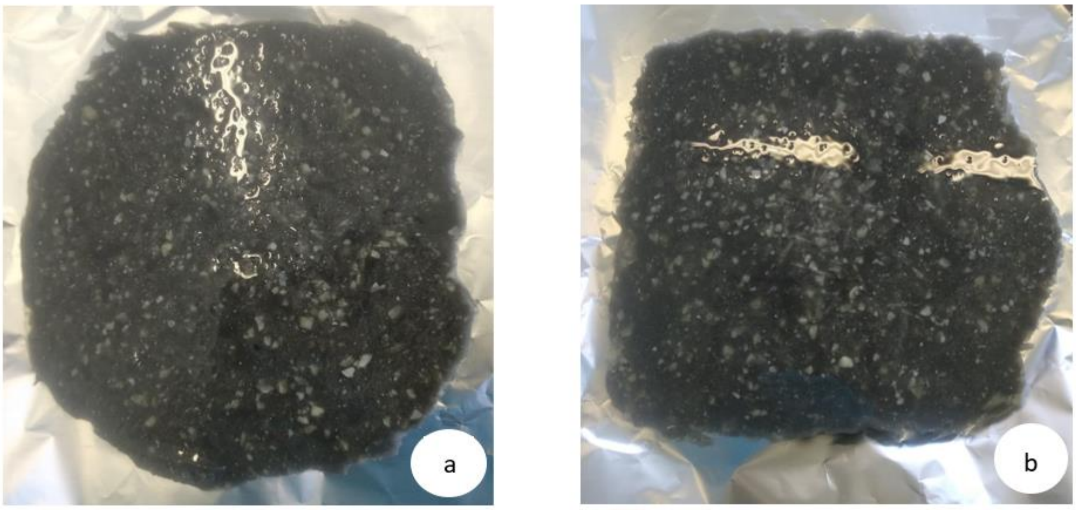


*Figure 98. Airbrush coating composite with the solution of AralditeBY158 and Aradur21 with previous pre-treatment surface (plasma and abrasive paper: a) 500 b) 400.*

In addition, instead of UV-curing, the curing of the coating was done at ambient temperature. The results remained poor. Another test was after coating phase, the composite with the coating solution was introduced into the stove at 100ºC for 1 hour but the result was failed.

Moreover, we try to produce small pieces made only from AralditeBY158 and Aradur21 without recycled fibre with the help of silicone moulds and we cover them by using the airbrush with a solution of the same composition in order to find out if our poor composite coating results are due to the technique used for the deposition of the coating solutions or if it is a problem of the surface of our recycled material. The curing was an ambient temperature. The result is shown in the following Figure 99:

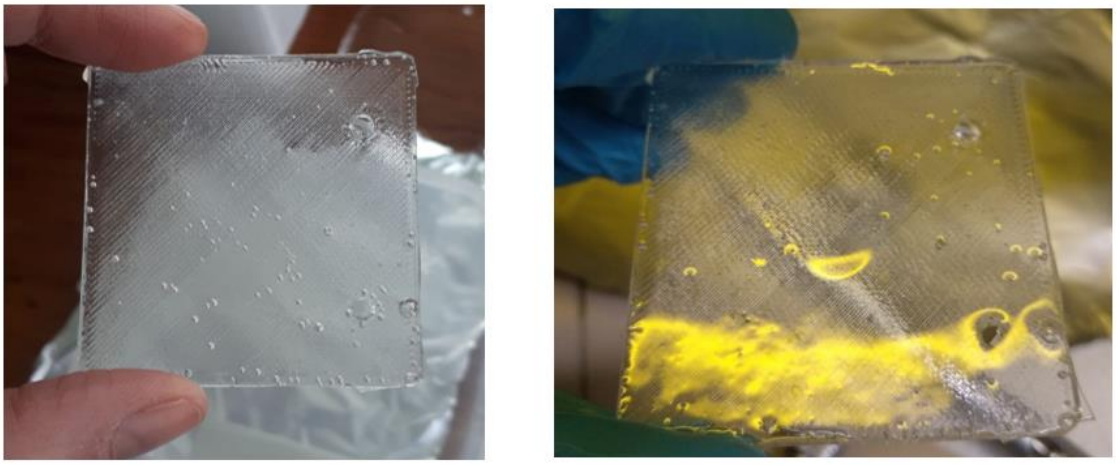


*Figure 99. Pieces of AralditeBY158 and Aradur21 before and after coating phase.*

From these results, we can see that the above poor results may be due to problems of compatibility of the coating solutions with our remanufactured material. There is a certain hydrophobicity between the surface of the composite and the coating solution.

### 4.3.6. Commercial epoxy primer.

Because of the poor results obtained from the coating of the remanufactured composite, it was decided to compare our results with the result of the application of a commercial epoxy primer as a coating for our pieces. The commercial epoxy primer used was the one shown in the Figure 100.

*Figure 100. Commercial epoxy primer.*

In this way, the result of the coating using a commercial epoxy primer on the surface composite was not good. It can therefore be concluded that the main difficulty about the surface finishing of this remanufactured material is due to the material itself and not to the coating solutions.

# 5. CONCLUSION

During the experimental development of this work, we have continued with the manufacture of samples of the new glass fibre reinforced polymer composites from recycle wind turbine waste in accordance with the specific measurements made in previous studies, that is, using 60% by weight of the recycled fibre due to its optimal properties. Therefore, we have managed to continue with the progress of achieving a circular economy by promoting the recycling of disused materials within the wind energy sector.

In this work, as a consequence of the importance within the field of composite materials, we have continued with the characterization of the surface of the recycled material as well as the study of the wettability of the system related to the contact angle that will have great repercussion during the coating stage.

Therefore, the second part of this project has been based on the study of the curing stage of polymeric composite materials. For this purpose, the manufacture of new coating resins has been investigated in order to optimize and improve the thermal and mechanical properties of the material, as well as to increase its life cycle.

After using different solutions of resins created from reagents such as commercial epoxy resin AralditeBY158, curing agents Aradur21, Succinic and Phthalic anhydrides with the commercial photoinitiator Omnicat440, measurements of UV-DSC and DSC were made to study their thermal properties: reactivity and Tg.

The results obtained after the UV-DSC, the value of the standardized integral, have shown that by increasing the concentration of the photoinitiator will increase the cross-linking power presented by the sample and therefore it will be more resistant to UV light.

On the other hand, the values obtained after DSC show the fundamental role played by the curing agent. The results obtained for solutions manufactured without curing agent require thermal pre-treatment in an oven at 100ºC so that sample cross-linking is fully achieved.

Of all the curing agents used, phthalic anhydride has obtained the best results. The curing agent Aradur21 inhibited the epoxy resin and the Succinic anhydride presented great miscibility difficulties. For this reason, they were discarded.

Subsequently, different application techniques were used for the deposition of the coating solution such as the use of a brush first, then the primer instrument and finally an airbrush with an ozone source. The best results were obtained with the use of an airbrush. However, in spite of performing a correct procedure during the coating stage having special interest to maintain the optimal cleaning conditions on the surface after the use of abrasive papers, solvents such as acetone or 2-propanol and plasma technology, the results have been unfavourable.

This result could be due to the fact that our remanufactured material has low wettability causing affinity problems between the coating resin and the surface of the recycled material.

Due to the current situation caused by the Covid-19 virus, the experiments proposed to achieve favourable results towards the optimum coating of this new recycled material could not be carried out.

Therefore, the main future prospect about the final surface finishing of this material will be to get the final recycled material to increase its wettability to achieve a homogeneous coating of the resin on the surface. Once this has been achieved, the next step will be to produce a piece with the 3D printer from the recycled glass fibre reinforced polymer composites.

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