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RECYCLING METHODS FOR FIBERS IN CARBON FIBER REINFORCED POLYMERS

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Acknowledgments

Here we are, the day has finally arrived. And what a journey these years have been!

If I look back on them, it seems as if time had flown by. But in the end I made it, I reached the goal of this fascinating course of study undertaken at the Politecnico di Torino.

It all started in 2015, when I, though a young and carefree student, had a fixed aim in mind: give my little but substantial contribution to make this planet a better place to live in

Today 14th October 2022, I have reached my finish line. With the achievement of my master's degree, I hope I have the knowledge and skills to be able to pursue the dream that has always accompanied me.

What wonderful years have they been, though not always welcomed by sunshine and paved with roses. Many difficult moments have I come across and had to face many challenging tasks, but those too have helped me made me the man I am today. Because of the outbreak of the Covid-19 pandemic, I was forced to take lessons online, return to my native land, continue my studies away from the friendly air of the Politecnico, its marvellous labs and the gatherings in the lecture theatres with my professors and university fellows. But I succeeded, despite the thousands drawbacks. De Andrè's words "flowers are born from manure" cheered me up and my fiancée encouraged me not to give up, strengthening our bond.

Here I am, at the end of the journey and I still can't believe it. But I am starting to realize that I succeeded, yes I did it, and already have years ahead, I hope, to a bright future to discover. However, all this would never have been possible if I had been alone, I would certainly have encountered more difficulties. Therefore, I feel the duty to thank those who have supported me along this wonderful trip.

First of all, the people who gave me the opportunity to write this thesis. Thanks to dear Prof. Monica Ferraris who has always been very helpful and kind in drafting this thesis, offering me the opportunity to tackle a slightly out-of-the-box but very interesting topic. Thanks to the supervisors Ing. Stefano De La Pierre Des Ambrois and Ing. Giuseppe Pipitone for their inexhaustible patience and availability. Thanks also to dear Prof. Giovanni Chiaramonte, who not only had the role of supervising the English syntax but who also gave me valuable advice on how to improve myself.

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I would also like to express a special thanks to those who are no longer here but who live in my heart, my grandparents, who would be proud of me and who knew that I would be able to crown every effort, believing in me even before I could only imagine it. I cannot forget to thank those who will never know they are being thanked in this thesis. A room is also dedicated to them. Thank you, my sweet and grumpy kitty daughter, Lady; thank you my lovely Frenchie puppy, Harley.

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Abstract

Thanks to their superior mechanical properties, Carbon Fiber Reinforced Polymers (CFRPs) are used as advanced materials in different sectors and their application has been extended from aerospace sector to automotive industry, sporting goods, renewable energy and construction. Therefore, the global demand of these type of material has seen an increase during the last years. Nevertheless, an increase of CFRPs production goes hand in hand with an increase of non-biodegradable waste, which are expected to be more than 263 ktons by 2030. Currently, unsatisfactory solutions are adopted for the disposal of these materials, since methods such as landfilling or incineration will lead to a serious environmental pollution. Unfortunately, to date, the literature does not present much content inherent to disposal of those type of materials, and the main technologies are not yet applied at the industrial level. Furthermore, also the production of carbon fibers lead to the pollution of the environment, since the carbon fibers manufacturing is an energy intensive process. Due to this, the recycling technique based on the reclamation of carbon fibers are continuously under innovative investigation. Therefore, thanks to this thesis, innovative and eco-friendly strategies for the disposal of CFRPs composite materials are defined and analysed in depth. These techniques are mechanical, thermal and chemical recycling. The first is based on crushing and milling the waste, while the other two on decomposing the waste by means of thermal (pyrolysis and fluidized bed) and chemical (solvolysis) processes. The properties and the composition of the recycled carbon fibers are discussed for each technique. While, at the end of the report, the most promising method is selected, discussing what can be recovered in energy terms and evaluating if the method can be sustainable.

Keywords: energy, renewable, sustainability, climate change, recycling, waste disposal, carbon fibers, composites, materials, hydrogen, CFRP.

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List of abbreviations

ΔT_m – Temperature logarithmic mean value

μ - Viscosity

A_{lat} – Lateral surface

CF – Carbon Fiber

CFRP – Carbon Fiber Reinforced Polymer

CLTE – Coefficient of Linear Thermal Expansion

CUT – Continuous Use Temperature

DBTT – Ductile to Brittle Transition Temperature

E - Young's Modulus

E_C – Composite Young's modulus

E_{cd} – Composite Young's modulus with discontinuous and randomly oriented fibers

E_f – Fiber Young's modulus

E_m – Matrix Young's modulus

EoL – End of Life

E_P – Particle Young's modulus

f_f – Fraction of fibers weight

f_m – Fraction of matrix weight

f_p – Fraction of particles weight

GFRP – Glass Fiber Reinforced Polymer

GHG – Green House Gas

GWP – Global Warming Potential

GWPA - Global Warming Potential impact of substituted products

GWPP – Global Warming Potential impact of process

GWPTOT - Global Warming Potential total of the system

HHV – Higher Heating Value

IEA – International Energy Agency

K – Fibers efficiency parameter

LCA – Life Cycle Assessment

LHV – Lower Heating Value

LPG – Liquefied Petroleum Gas

MM – Molecular Weight

NPV – Net Present Value

OC – Operation Cost

p – Pressure

PAN – Polyacrylonitrile

Q_{loss} – Heat loss at the reactor

Q_{py} – Heat required to heat up the material during pyrolysis

r-CF – Recycled Carbon Fiber

RES – Renewable Energy Source

SCF – Supercritical Fluid

SCW – Supercritical Water

SEM – Scanning Electron Microscopy

T – Temperature

T_G – Glass Temperature

T_M – Melting Temperature

T_S – Softening Temperature

TS – Tensile Strength

U – Overall coefficient of heat-transfer

UCF – Average cost per mass unit of recovered fiber

UCW – Average cost per mass unit of waste

v-CF – Virgin Carbon Fiber

VdW – Van der Waals

wt%- Weight percentage

XPS – X-ray Photoelectron Spectroscopy

ε – Strain

σ_y – Yield Strength

η – Energy efficiency of pyrolysis

1. Introduction

What is energy? In the roughest physical term, energy is the capacity to do work. However, it might not be an exaggeration to think that energy is the key aspect of life all around the Universe. Something like an infinitesimal part of nothing compared to man's greatest masterplan. Surely, energy is a priceless source for mankind. As a matter of fact, human civilization has always needed energy to grow and develop through the centuries. Starting from the beginning with the capability of controlling and consuming energy with fire and animal force, up to today in which energy is exploited in the best possible way and diffused in every aspect of our daily life.

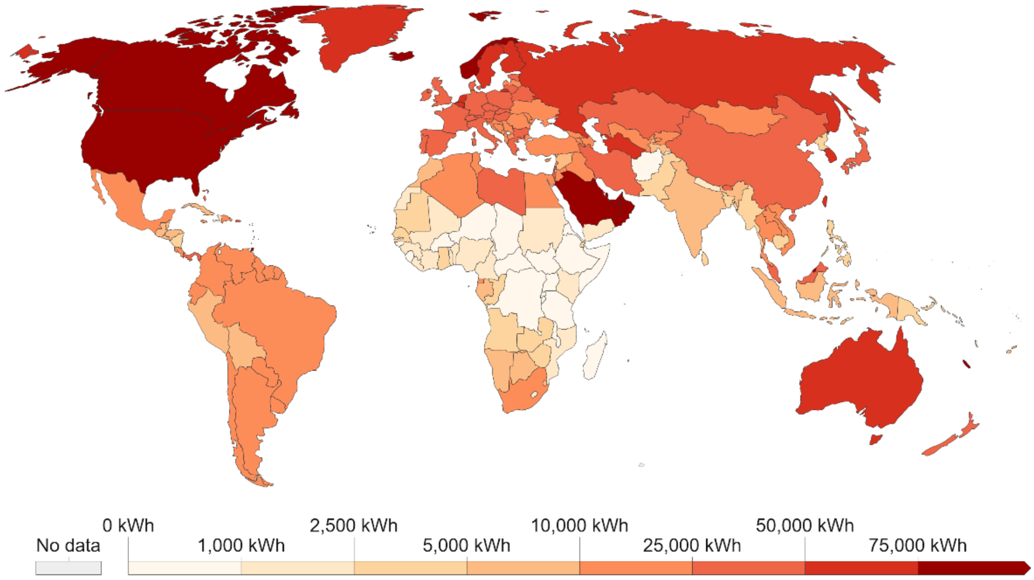


Figure 1-1: Energy use per person in 2021 [1](electricity, energy consumed for transport, heating, and cooking)

Obviously, the presence of more sources of energy available goes hand in hand with the possibility of accessing multiple benefits, from keeping constantly charged domestic appliances to living in a comfortable and well heated home during rigid winters. Nevertheless, in the last decades a gradual increase of the living standards and a demographic growth have led to an abrupt increase in energy demand throughout the globe. This growing request is mainly satisfied in the easiest way, resorting to traditional commodities such as fossil fuels, which are exploited to an outstanding level. Unfortunately, taking into account the dear old "lex talionis", there is a price to pay, namely an excessive amount of pollutant which has been injected in the environment since the first Industrial Revolution. It is true that the environmental pollution is not only caused by anthropic activities, but also by natural causes. However, the production of GHG (Green House Gases), CO_2 and other damaging chemical compounds, is strictly linked to the combustion of fossil fuels. This pollution has led to the biggest challenge that the humanity has ever seen: the fight against Climate Change. This is the biggest crisis that the entire world has ever faced, and it requires a rapid and concrete cooperation on a global scale. As Bill Gates stated in one of his most famous books: "To sum up: we need to accomplish something gigantic we have never done before, much faster than we have ever done anything similar" [2]. Unfortunately, it seems clear that at present the current approaches are not enough (Figure 1-2).

As an example, the “Overshoot Day”, the day that humanity’s demand for ecological resources exceeds the resources Earth can regenerate within that year, is running faster and faster. In the current year it fell on July the 28th, while last year (2021) on July the 29th [3]. This is a big deal considering that in 1970 the Overshoot Day occurred on December the 30th. “Earth provides enough to satisfy every man’s needs, but not every man’s greed” [4]. In fact, this phenomenon affects every existent sector, and requires sudden and clear actions, since in the long run the Climate Change can lead to catastrophic events. At present, the COP (Conference of Parties) to the UNFCCC (United Nations Framework Convention on Climate Change) provides critical crucial actions and goals as a response to climate change (see [6] for further information).

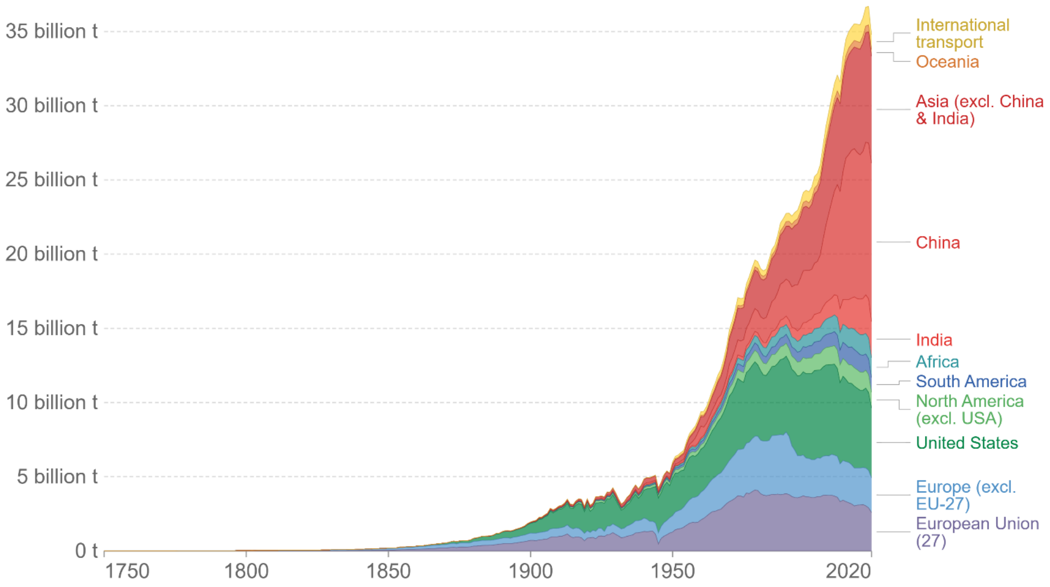


Figure 1-2: Annual CO_2 emissions from fossil fuels, by world region [5]

The IPCC (Intergovernmental Panel on Climate Change) highlights that Earth’s average temperature has increased by 1,1°C and there are around 11 years for limiting the emission to maintain the increasing temperature under 1,5°C at the current rate of emission (Figure 1-3).

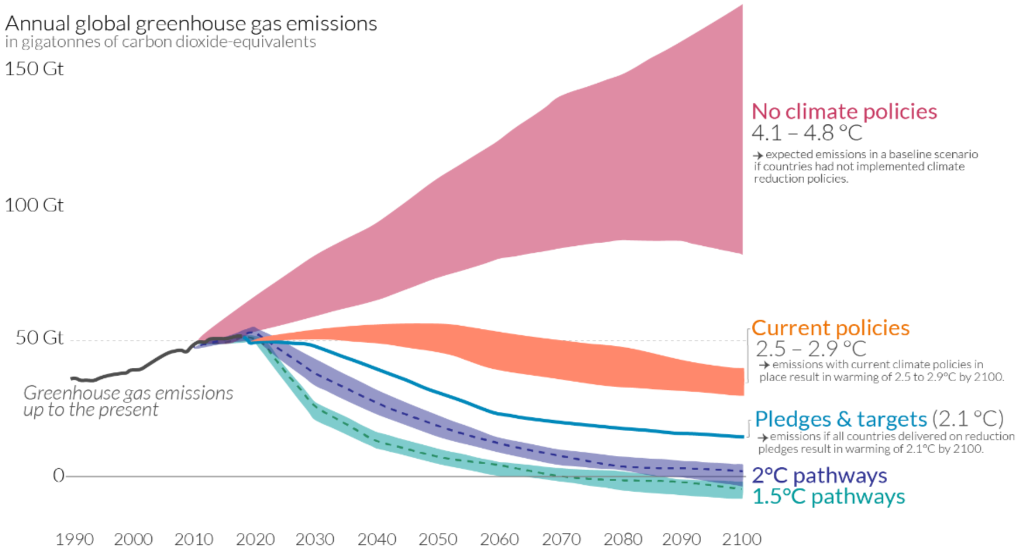


Figure 1-3: Global GHG emissions and warming scenarios [5]. Each pathway comes with uncertainty, marked by the shading from low to high emissions under each scenario. Warming refers to the expected gloabal temperature rise by 2100, relative to pre-industrial level.

As for the previous years (as it can be seen in Figure 1-4), the greatest portion of $CO_{2,eq}$ is produced by the "Electricity and heat" sector. Therefore, it seems clear that the most obvious change should be the shift from the conventional commodities to the Renewable Energy Sources – RES.

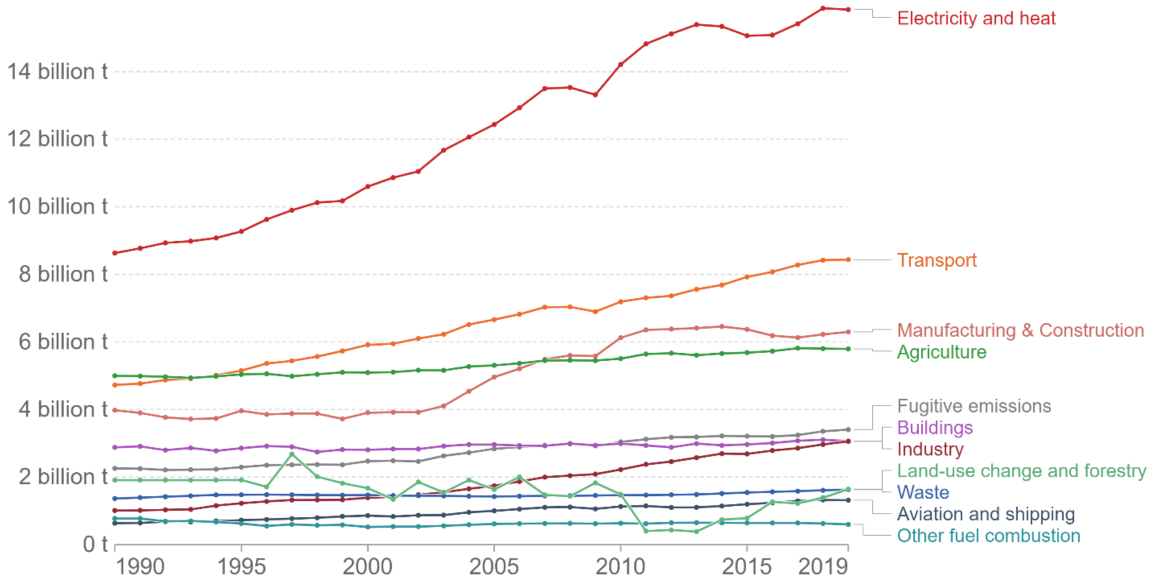


Figure 1-4: GHG emissions by sector in the World [7]. Emissions measured in CO2eq.

Clearly, they can represent a huge step in the fight against Climate Change, producing energy thanks to natural sources (sun, wind, geothermal, hydroelectric, ocean and so on). The introduction of RES is not as easy as can be imagined, since it is true that they introduce many advantages (mainly relative to the environment), but they are also accompanied by several limitations if compared to the fossil fuels. The most striking example is that these RES are not a continuous source of energy, as the energy output is not constant and sometimes random in the medium term, leading to a challenge in the matching between demand and energy offer. Nevertheless, thanks to the British Petroleum (BP) Statistical Review of World Energy [8], the contribution of RES in the world primary energy consumption can be appreciated (Figure 1-5).

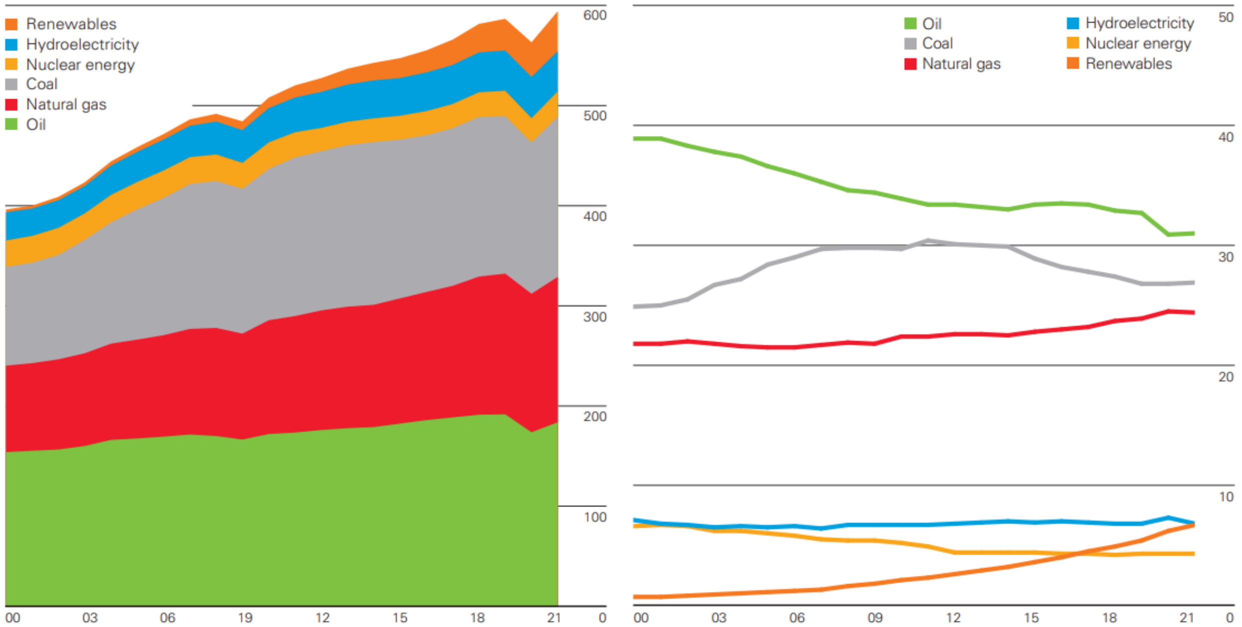


Figure 1-5: World consumption (left) measured in exajoule. Shares of global primary energy (right) measured in percentage. [8]

1.1 Purpose of the research

As it has been said in the abstract, the main aim of this report is to investigate the most innovative and eco-friendly strategies that permits an affordable disposal of the Carbon Fibers Reinforced Polymer – CFRP composite materials. These types of reinforced materials are becoming more widespread in different sectors, from sporting goods to industrial products. In fact, they can show superior properties (fully explained in the following chapters), which allow them to replace commonly used materials. Yet, the CFs' production and EoL phases of their lifecycle reveal a consistent environmental impact, higher than the pollution generated for metals manufactory. Hence, with the term "disposal" it is meant the reclamation of CFs, since the recycled ones have significant less GWP if compared with the virgin CFs. A study conducted by the "Fraunhofer Institute for Environmental, Safety and Energy Technology" determined that the GHGs emissions for v-CFs are of 29.45 metric tonnes CO_2 per tonne of v-CF, compared with an average of 4.65 metric tonnes CO_2 per tonne of r-CF [9]. The aim of this thesis is mainly to raise awareness on a sustainable disposal of CFRPs, analysing in depth each actual technology that permits the reclamation of CF from the polymeric matrix, in order to save a huge amount of pollutant that would be injected continuously with the common methods applied for their disposal.

2. Polymers

Polymers are a type of advanced materials that are widely used in almost every dominion of our daily life, from industrial and scientific applications to clothing and utensils manufacturing. As it is said in [10], the impact of those materials on the present lifestyle is incalculable, just have a look around to notice that they are everywhere: "clothing made from synthetic fibres, polyethylene cups, fiberglass, nylon bearings, plastic bags, polymer-based paints, epoxy glue, polyurethane foam cushion, silicone heart valves, and Teflon-coated cookware. The list is almost endless" [10].

There are two types of polymers: natural and synthetic (see Figure 2-1). Synthetic polymers are derived from fossil sources (oil) such as polyethylene, polyester, Teflon and epoxy. Natural polymers can be extracted from natural sources such as DNA, cellulose and proteins. In the example, as it can be read from [11], proteins are polymers of 20 different types of amino acids. Nucleid acids carry genetic information and cellulose/resins build the solid parts of plants. As for the synthetic ones, the "Bakelite" was the first synthetic thermoset polymer obtained in 1907 from Baekaland through the polycondensation of phenol with formaldehyde (PF) [12].

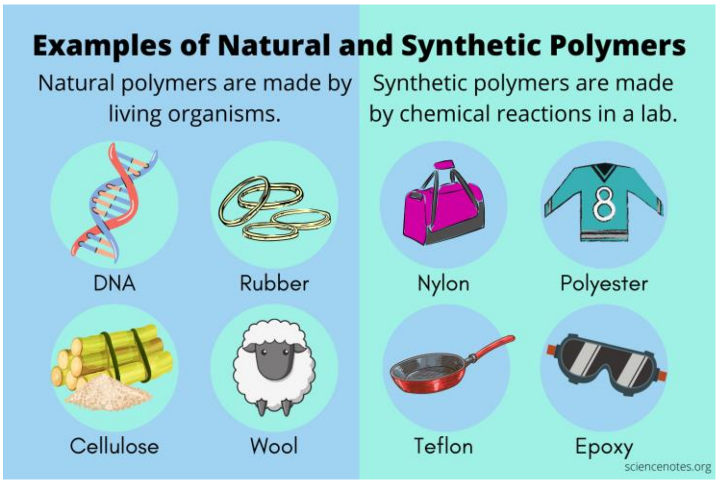


Figure 2-1: Example of natural and synthetic polymers [15]

Due to the obvious necessity to replace the classical materials, the polymer industry has seen a rapid growth, introducing facilitations and comforts that have set the idea that it is unthinkable to live without them. Let's have a look at Figure 2-2 to understand the worldwide and local production of polymers (intended as plastic materials).

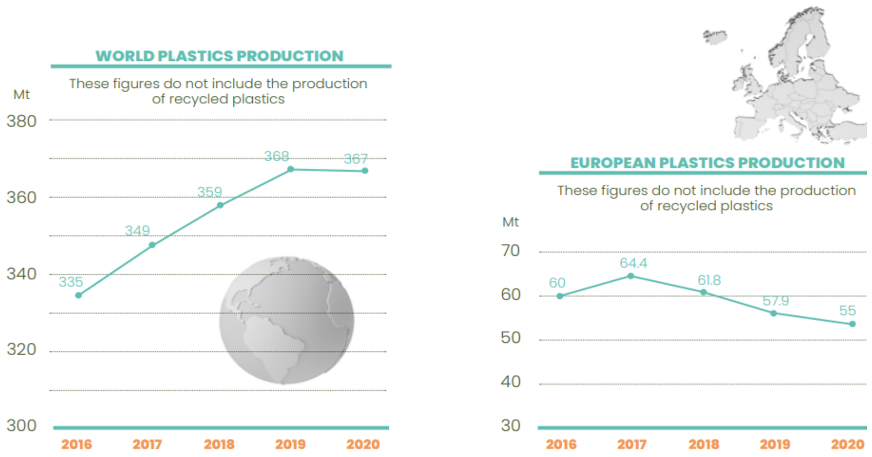


Figure 2-2: World and European plastic production [13]

2.1 Molecular structure

The word “polymer” comes from the Greek /ˈpɒlɪmər/; Greek poly-, "many" + -mer, "part" [14] and they are long organic macromolecules with a “zig-zag backbone” structure (see Figure 2-3), often called “spaghetti structure”, composed by the repetition of a single repeating unit, which are monomers.

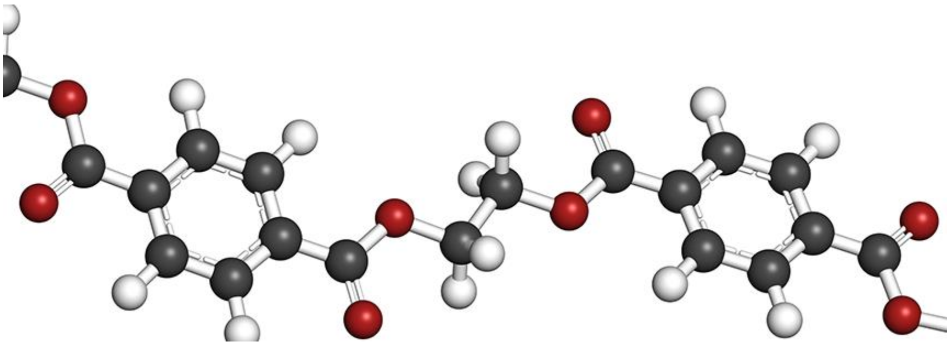


Figure 2-3: Polymer molecular structure [16]

Those materials are characterized by a low density, less than $1\ ^{g}/_{cm^3}$, and due to their properties can also be good insulators for sound, heat and electricity. As it will be explained in the following chapters, they do not show good thermal and mechanical properties, and this is the reason why they are reinforced with the carbon fibers forming the Carbon Fibers Reinforced Polymers (CFRPs).

Different monomers can give birth to different polymers (see Figure 2-4) and can be coupled together by means of a chemical reaction called “polymerization” [17]. There are two different types of this process:

- Addition/Chain-reaction polymerization - whatever precursor can be coupled to the monomer once the double bonding between two C atoms is broken, the chain grows one monomer at a time.
- Condensation/Step-reaction polymerization - molecules join losing small molecules as by-product such as water (water bottles made of PET are based on this process), the polymer chain doubles with each step.

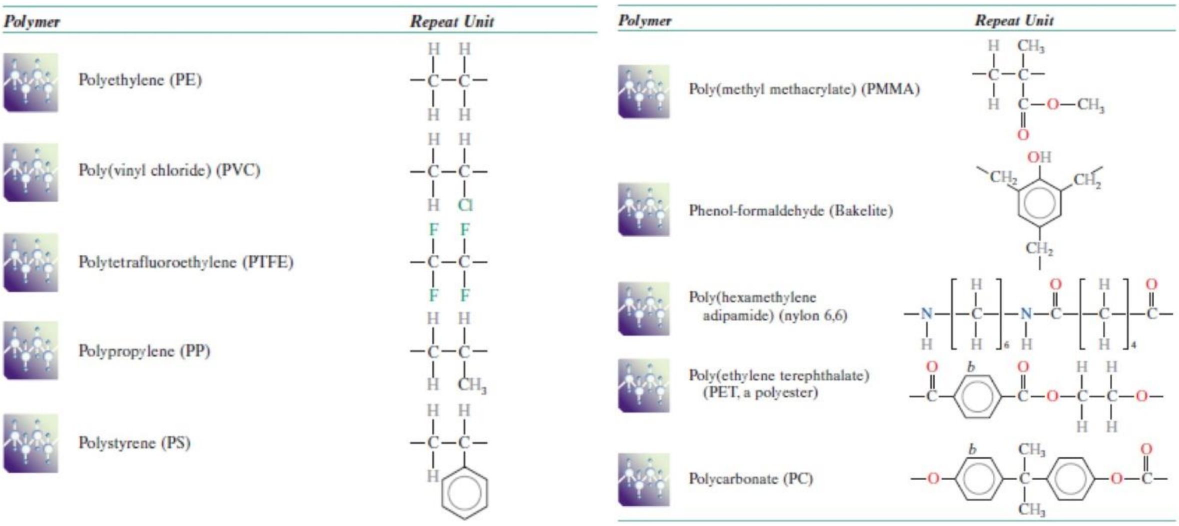


Figure 2-4: List of Repeat units of the 10 most common polymeric materials [18]

The physical properties are strictly related to their disordered crystalline structure, due to this they are classified as amorphous materials. That means that these materials do not have a precise melting temperature, at which the phase change between solid and liquid occurs. However, they are characterized by a softening point and by a glass transition temperature T_G, at which they can be easily machined thanks to the viscous liquid or rubber like behaviour. In this case, the viscosity curves are very helpful (μ vs. T).

As for bondings between molecules, we can distinguish between primary and secondary bondings:

- Primary bondings – occur in the side chain and are mainly of the covalent type.
- Secondary bondings – weaker than the primary ones of three orders of magnitude, and are of the Van der Waals type. They occur because of the different polarity of the elements inside the chain.

Therefore, different bondings can lead to the formation of different types of polymers, more specifically they can be thermoplastic or thermoset polymers and the distinction between these two types of polymers must be clarified, since they have very different properties, application and EoL treatments.

The thermoplastic polymers are characterized by the presence of primary bondings only in the side chain, while the secondary ones can occur between different chains because of different polarity. The picture in Figure 2-5 can clarify the distinctions. “A thermoplastic is any plastic material which melts into a soft, pliable form above a certain temperature and solidifies upon cooling. Thermoplastics can be re-melted and re-shaped any number of times. They are usually stored in the form of pellets prior to the moulding process” [19]. It seems clear that in term of sustainability the main advantage consists in the recyclability. Common examples of thermoplastic polymers are acrylic, polyester, polypropylene, polystyrene, nylon and Teflon. These behaviours can be understood better by looking at the viscosity curve in which the viscosity abruptly decreases with the increasing temperature.

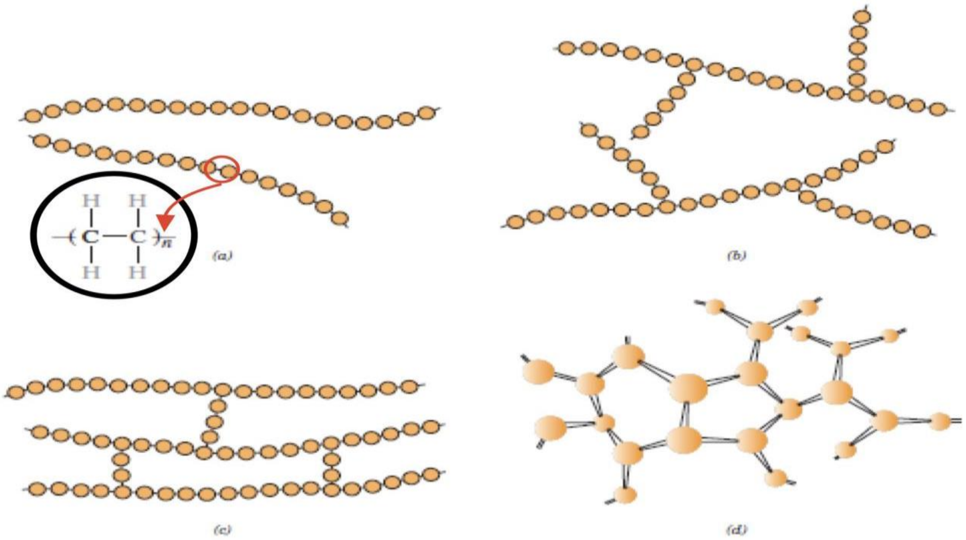
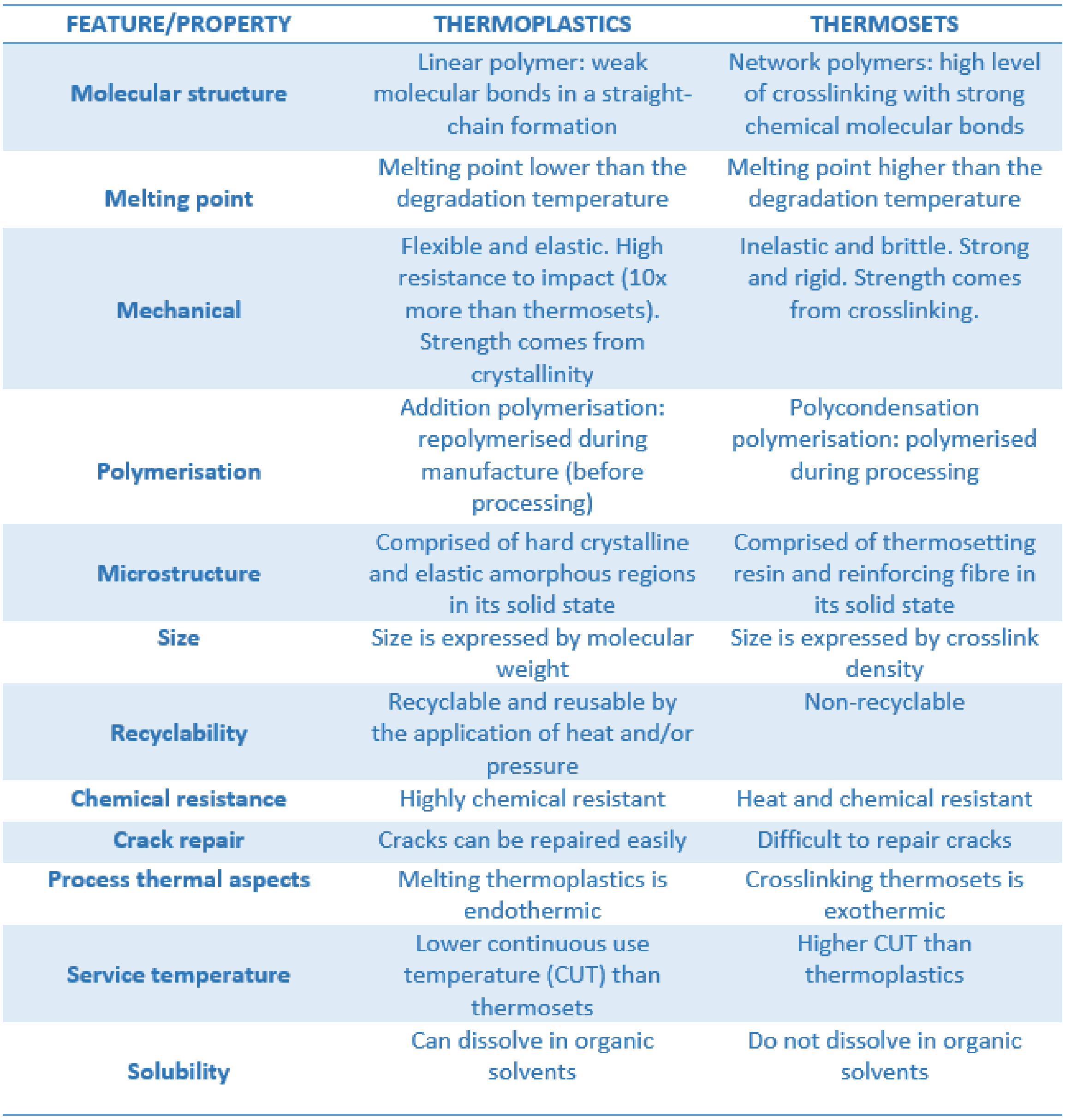


Figure 2-5: Schematic representation of (a) linear, (b) branched, (c) cross-linked and (d) 3D structures. Circles designate individual monomers [18]

In the thermosets, the different chains are cross-linked since the primary bondings occur also between them (Figure 2-5). According to [19], thermosets "remain in a permanent solid state after being cured one time. Polymers within the material cross-link during the curing process to perform an unbreakable, irreversible bond. That means that thermosets will not melt even when exposed to extremely high temperatures." Compared to the thermoplastics, they expose much better mechanical properties. On the contrary, they cannot be recycled but instead could be burdened or shaped into pellets, incinerated or reduced to the initial molecules in appropriated chemical plants. This argument will be treated properly in the next chapters as one of the main focuses of this work. Examples of thermosets are epoxy, silicone, polyurethane and phenolic. They are stored in liquid phase inside large containers [19].

The main differences between thermoplastic and thermoset polymers can be summarized in the following table (Table 2-1) which is extracted from [20]and rearranged.

Table 2-1: Thermoplastics vs. Thermosets [20]



FEATURE/PROPERTY	THERMOPLASTICS	THERMOSETS
Molecular structure	Linear polymer: weak molecular bonds in a straight-chain formation	Network polymers: high level of crosslinking with strong chemical molecular bonds
Melting point	Melting point lower than the degradation temperature	Melting point higher than the degradation temperature
Mechanical	Flexible and elastic. High resistance to impact (10x more than thermosets). Strength comes from crystallinity	Inelastic and brittle. Strong and rigid. Strength comes from crosslinking.
Polymerisation	Addition polymerisation: repolymerised during manufacture (before processing)	Polycondensation polymerisation: polymerised during processing
Microstructure	Comprised of hard crystalline and elastic amorphous regions in its solid state	Comprised of thermosetting resin and reinforcing fibre in its solid state
Size	Size is expressed by molecular weight	Size is expressed by crosslink density
Recyclability	Recyclable and reusable by the application of heat and/or pressure	Non-recyclable
Chemical resistance	Highly chemical resistant	Heat and chemical resistant
Crack repair	Cracks can be repaired easily	Difficult to repair cracks
Process thermal aspects	Melting thermoplastics is endothermic	Crosslinking thermosets is exothermic
Service temperature	Lower continuous use temperature (CUT) than thermosets	Higher CUT than thermoplastics
Solubility	Can dissolve in organic solvents	Do not dissolve in organic solvents

While in Table 2-2 and Table 2-3, as for Table 2-1, the most common types of materials are summarized for sake of simplicity.

Table 2-2: Thermoplastic materials [20]

THERMOPLASTIC	PROPERTIES AND APPLICATIONS
Polyamide (nylon)	Tough and relatively hard material used for power tool casings, curtain rails, bearings, gear components and clothes
Polymethyl Methacrylate (PMMA, acrylic)	Stiff, durable and hard plastic that polishes to a sheen, used for signage, aircraft fuselage, windows, bathroom sinks and bathtubs
Polyvinyl Chloride (PVC)	Tough and durable material that is commonly used for pipes, flooring, cabinets, toys and general household and industrial fittings
Polypropylene	Light, yet hard material that scratches fairly easily, with excellent chemical resistance, used for medical and laboratory equipment, string, rope and kitchen utensils
Polystyrene (PS)	Light, stiff, hard, brittle, waterproof material used mainly for rigid packaging
Polytetrafluoroethylene (PTFE, Teflon)	Very strong and flexible material used for non-stick cooking utensils, machine components, gears and gaskets
Low-density Polythene (LDPE)	Tough, relatively soft, chemical resistant material used for packaging, toys, plastic bags and film wrap
High-density Polythene (HDPE)	Stiff, hard, chemical-resistant material used for plastic bottles and casing for household goods

Table 2-3: Thermoset polymers [20]

THERMOSET	PROPERTIES AND APPLICATIONS
Epoxy resin	Hard material that is brittle without extra reinforcement. Used for adhesives and bonding of materials
Melamine formaldehyde	Hard, stiff and strong, with decent chemical and water resistance, used for work surface laminates, tableware and electrical insulation
Polyester resin	Hard, stiff and brittle when unlaminated. Used for encapsulation, bonding and casting
Urea formaldehyde	Hard, stiff, strong and brittle used primarily in electrical devices due to its good electrical insulation properties
Polystyrene (PS)	Light, stiff, hard, brittle, waterproof material used mainly for rigid packaging
Polyurethane	Hard, strong and durable material used in paint, insulating foam, shoes, car parts, adhesives and sealants
Phenol formaldehyde resin (PF)	Strong, heat and electrical-resistant material used in electrical items, sockets and plugs, car parts, cookware and precision-made industrial parts

An important characteristic of polymers, which directly affects their physical properties, is crystallinity. Polymers are able to undergo crystallisation by forming crystalline or (more often) semi-crystalline structures. Crystalline polymers are formed by the packing of the chains in order/aligned arrays. For instance, in Figure 2-6 an illustration of the complex polyethylene chains structure is shown, packed in an ordered fashion to give a polyethylene unit cell.

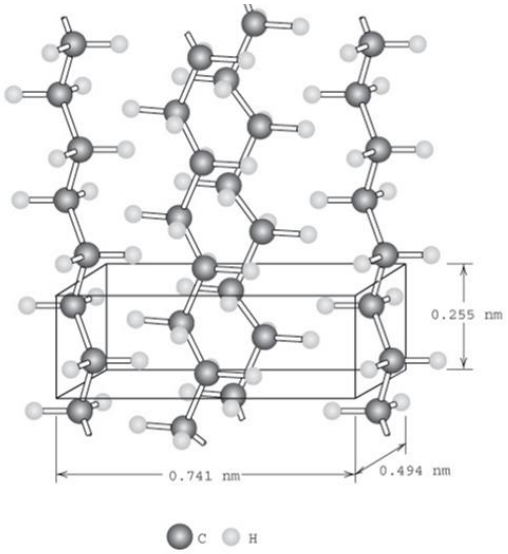


Figure 2-6: Disposition of the molecular chains of polyethylene in a single cell [17]

The cooling rate during the solidification phase will directly affect the crystallisation of the material since a sufficient amount of time is needed to almost perfectly align the polymeric chains. It seems clear that a too fast cooling with a phase change from liquid to solid will lead to an imperfect crystallisation. Obviously, polymers composed by simpler repeating unit are able to crystallise a way faster than other with more complex structures.

In most of the cases, because of the large polymeric chains, the structure tends to be only partially crystalline, with amorphous regions that separate the ordered parts of the structure. Therefore, semicrystalline polymers consist of small crystallites embedded in an amorphous matrix. In Figure 2-7 the structure of spherulites can be appreciated, which is a spherical structure formed from the controlled cooling of a molten polymer, containing lamella chain-folded crystallites, surrounded by amorphous regions.

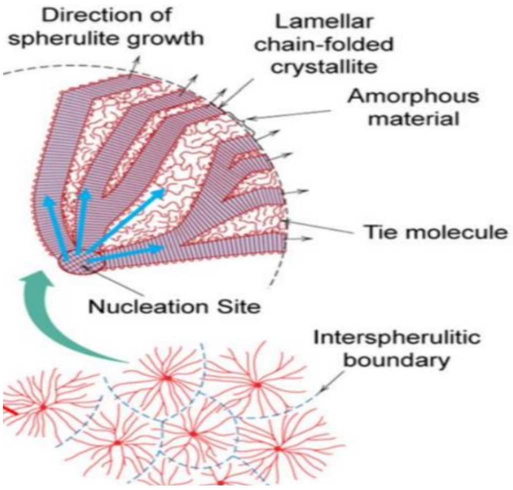


Figure 2-7: Spherulitic structure of a semi-crystalline polymer [17][17]

2.2 Moulding techniques

Searching through literature and on the internet, it is possible to appreciate that there are several different techniques commonly used to form polymers. Each of them strictly depends on whether is thermoplastic or thermoset. "Thermoplastics are melted from a solid and reshaped before cooling. Common forming methods include injection moulding, blow moulding and extrusion. Thermosets are not fully polymerised before forming. They are formed into the desired shape and then made into a solid through a chemical reaction to create cross-links in the polymer chains. Common forming methods include injection moulding, compression moulding and transfer moulding" [21]. Some information about the different moulding techniques were collected and a brief overview on each of them can be reported.

Starting from the "Extrusion Moulding" [22], the hot melted raw material is pressed through a die, a shaped hole through which the molten polymer is pressed to obtain a lengthy shaped component (Figure 2-8). The other techniques also use the extrusion. The difference relies in the fact that the others use a mould to obtain the desired shaped polymer while the extrusion moulding obtain the shape in function of the die's one. This moulding technique is low cost due to the simple equipment and can produce components with the same shape along the length of it, such as straws or PVC pipes.

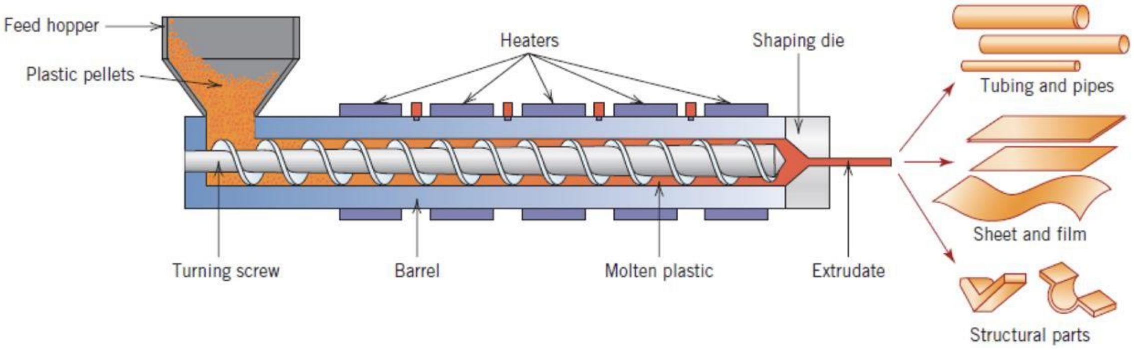


Figure 2-8: Schematic diagram of an extruder [17]

When the aim is to obtain a uniform wall thickness, the best choice is to use the "Blow Moulding" [22] technique, able to give a hollow and thin-walled outcome. Literally it is like blowing air into a balloon. The plastic is put inside a shaped mould and then air is blown letting the plastic grow bigger until the mould walls are covered to take its shape (Figure 2-9). Then the product is cooled to keep its shape. This is a very fast (1400 product per 12 hour a day) and economically friendly, responsible for the production of bottles, cases and also fuel tanks.

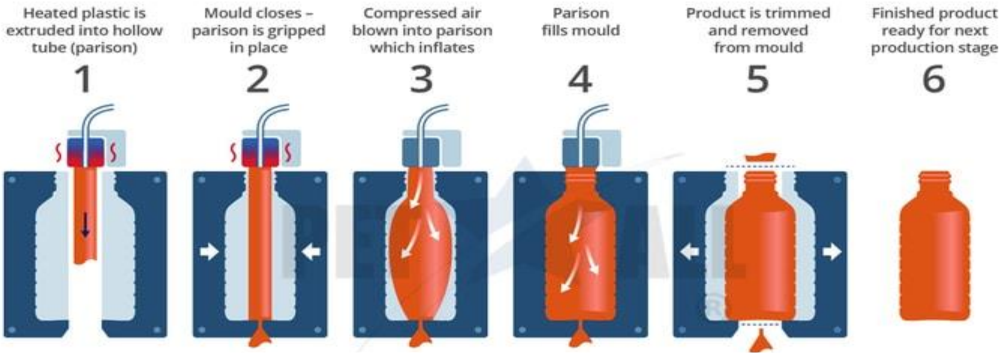


Figure 2-9: Schematic diagram of a blow moulding technique [23]

If a strong and durable component is needed to substitute, as an example, a broken metallic part, the "Compression Moulding" [22] can be very useful. This technique consists in the pouring of the liquid raw polymer into a shaped mould which is kept heated in order to compress the material obtaining the desired product (Figure 2-10). Thanks to the high temperature, the final product, removed from the mould after being cooled down, has high strength even if it is a plastic. Generally, the cost per part with this technique is low, but the cost-effectiveness depends on the mould design and machinery complexity.

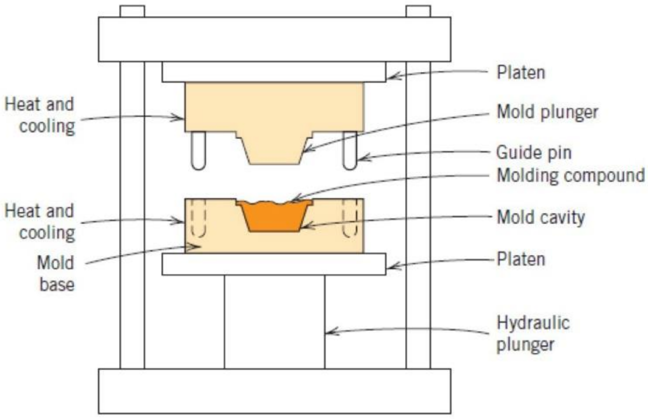


Figure 2-10: Schematic diagram of a compression moulding apparatus [17]

There are some situations in which high volume components are needed, such as in the aerospace and automotive fields or also for medical equipment. In these cases, the grand-daddy of the mass production processes can be introduced, and it is the "Injection Moulding" [22]. The process is like the Extrusion Moulding, with the difference that the molten raw material is pressurized directly into a shaped mould (Figure 2-11). Once it is filled, the polymer is cooled to keep its new shape and the mould is opened. This technique can satisfy the need of the designers with high flexibility. Concerning the moulds, they can be very expensive since they are made of steel or aluminium to ensure good thermal/mechanical properties. Nevertheless, the cost per production unit falls in function of the production volume.

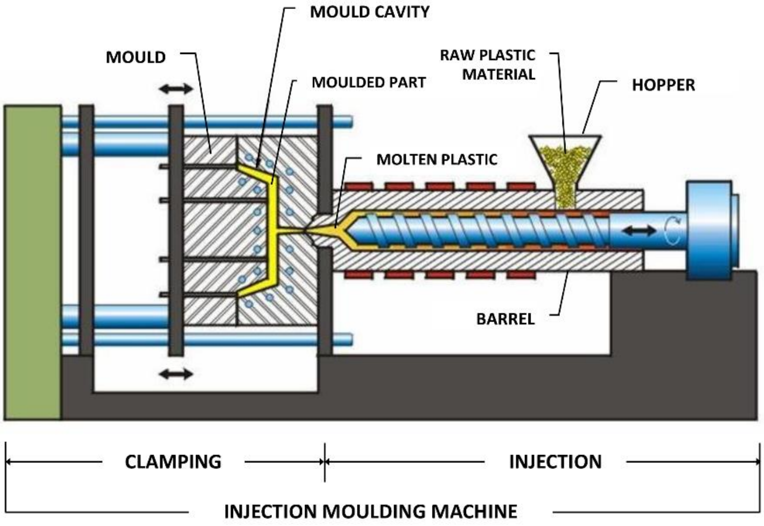


Figure 2-11: Schematic diagram of an injection moulding apparatus [24]

When large and hollow parts have to be produced, like car components or storage tanks, the most suitable technique is the “Rotational Moulding” (aka “rotomoulding”) [22]. In this case, the moulds’ design is flexible letting the component being able to change the shape of the final product. The polymer, that could be a resin or a molten one, is placed into the mould, which is kept at high rotational speed, so that the material can cover the whole surface, leading to the formation of a hollowed part with thin walls (Figure 2-12). Therefore, the mould is cooled, and the final shaped product is obtained. It can be said that this is an environmental-friendly process since it is material efficient and economic, leading to lower start-up costs (compared to the other processes) and to efficient production, even at low volume production.

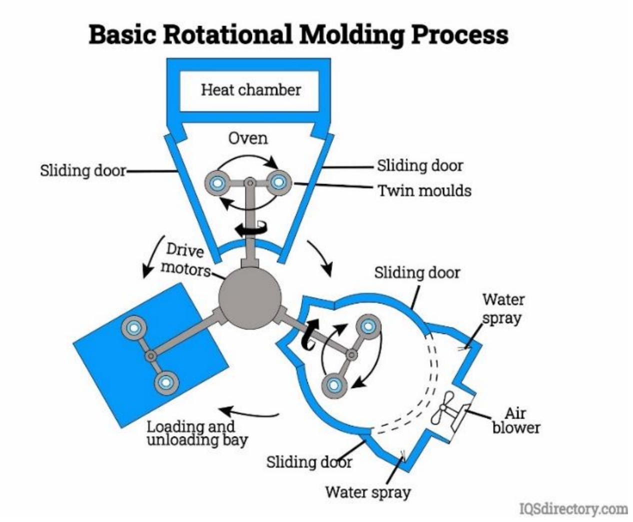


Figure 2-12: Schematic diagram of a rotational moulding apparatus [25]

When more intricate design should be realized, “Reaction injection moulding” [26] can be applied. Commonly used in the automotive industry for the lightweight components, strong and yet flexible. Reaction injection moulding uses two elements combined and injected into the hot mould. They are thermoset polymers injected into the mould through a pressure injector that works at roughly ambient temperature (Figure 2-13). The downside relies in the non- recyclability of the product. The costs are a bit higher than the ones for the injection moulding, because of the more expensive raw materials.

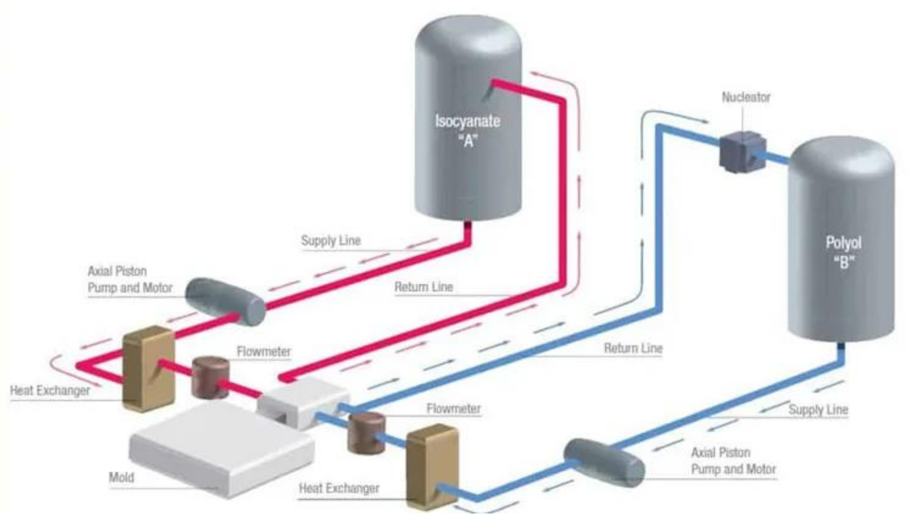


Figure 2-13: Schematic diagram of a reaction injection moulding apparatus [27]

Sometimes a reasonable amount of product of high-quality must be produced without necessarily large investments on materials and machinery. In this case the best choice should be the “Vacuum casting” [26]. A master pattern with a high-quality surface finish is used to produce the silicon mould by casting the silicon on the patter under vacuum condition to avoid the formation of bubbles. Then, after curing it, the silicon mould is cut and the master pattern is removed, leaving a cavity to produce components with the same shape (Figure 2-14). The disadvantages consist in the fact that the moulds are not durable and degrade after more or less 20 copies.

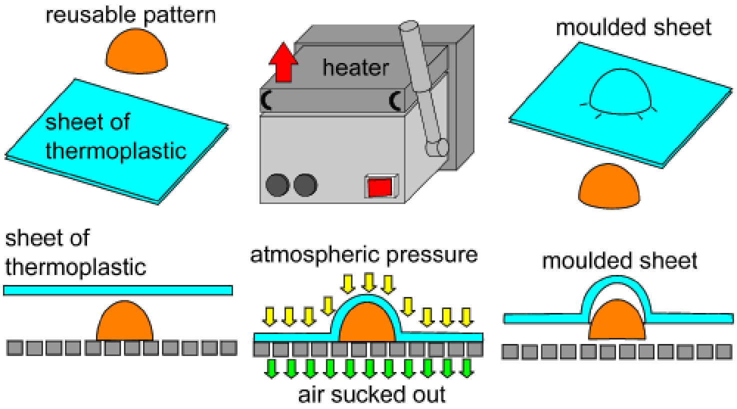
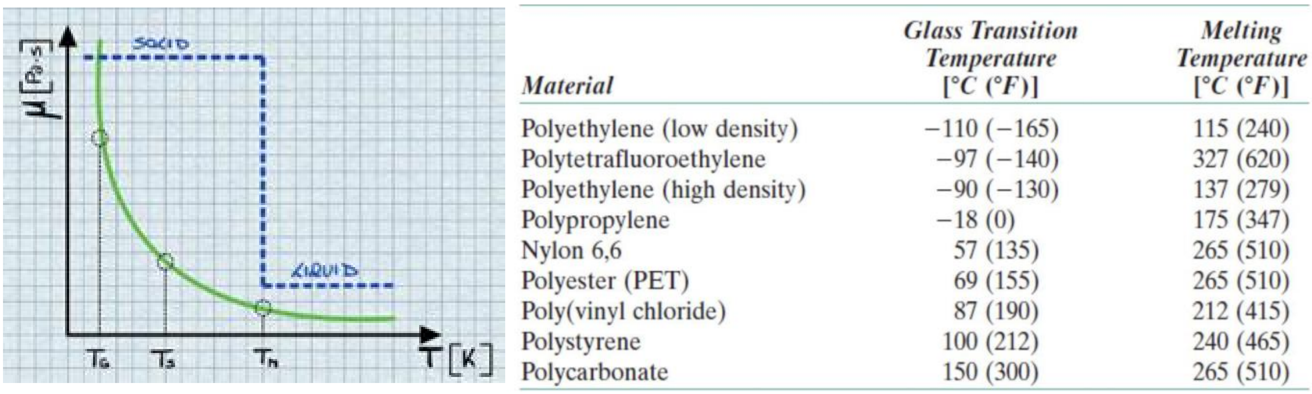


Figure 2-14: Raw schematic for Vacuum casting [28]

2.3 Physical Properties

In this paragraph the properties of those material will be focused. As said above, they do not have a precise melting temperature, due to their disordered lattice. They are treated as amorphous materials, which means that at a certain temperature they pass from a solid state to a rubbery like one, and further they will reach the softening temperature at which they act as a viscous liquid, able to be shaped, machined or recycled. The T_G depends on the capability of the chain to rotate along the chain backbone of the polymeric chain. This behaviour can be highlighted in the viscosity curve below, remembering the differences between a thermoplastic and a thermoset polymer (Figure 2-15a), and reporting some numbers as an example, specifying that the T_S lies always between the T_G and the T_M (Figure 2-15b).



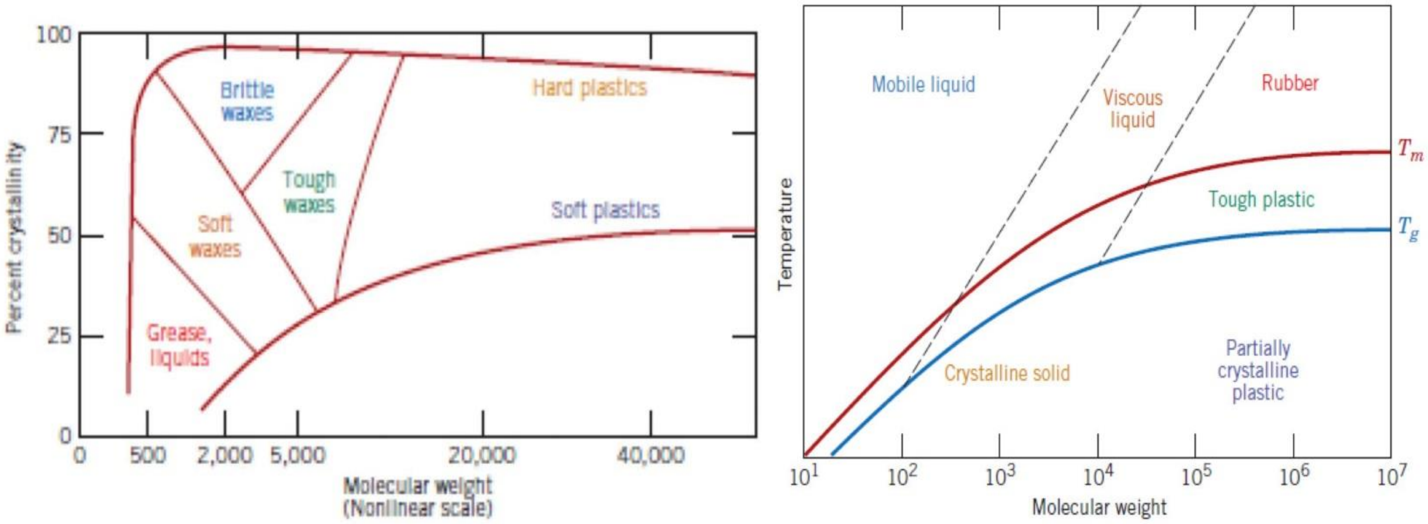
Material	Glass Transition Temperature [°C (°F)]	Melting Temperature [°C (°F)]
Polyethylene (low density)	−110 (−165)	115 (240)
Polytetrafluoroethylene	−97 (−140)	327 (620)
Polyethylene (high density)	−90 (−130)	137 (279)
Polypropylene	−18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

(a

(b

Figure 2-15: Scratch of a viscosity curve for amorphous/crystalline materials (a) (handmade) and melting/ glass temperatures for some of the most common polymeric materials (b) [18]

The choice of the polymeric material can be done in function of its molecular weight. In fact, decreasing or increasing the length of the polymeric chain will directly change the properties of the material, affecting in example the temperature and crystallinity (Figure 2-16a, b), with the possibility to pass from a hard plastic to a rubber like one. Having a clarifying example, considering polyethylene $2(\mathrm{CH_2})_n$, a single repeating unit weights $28\ {}^{\mathrm{g}}/_{\mathrm{mol}}$, so the properties of the material will be directly affected by the number of monomers composing the chain.



(a   (b

Figure 2-16: Dependence of polymer properties as well as degree of crystallinity (a) and melting/glass transition temperatures (b) on molecular weight [17]

When the T_G is lower, the molecules can displace easily and so the glassy state can be converted to the rubbery one at low T. Otherwise, if the mobility of the chains is restricted, the glassy state is more stable since more energy is required to make the chains free. That means that the T_G is increased. This behaviour can be highlighted in the Figure 2-17.

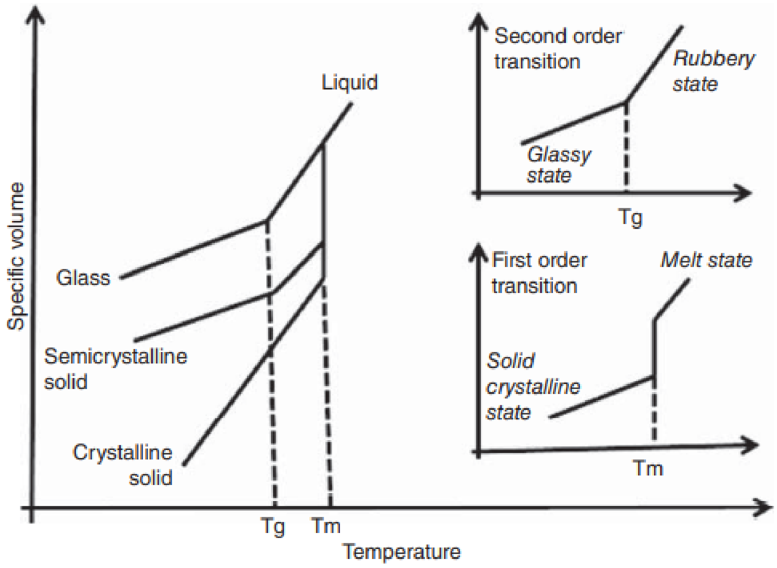


Figure 2-17: Melting point and glass transition temperature of polymer [29]

In various papers, the glass transition temperature is linked to a simple formula that relates the T_G to the molecular weight of the polymeric chain (Figure 2-18). This is the Fox-Flory equation, and the clearer explanation can be found in [30]:

$$T_G = T_{G,\infty} - {}^{K}/_{MM_n} \tag{1}$$

In Equation 1 "$T_{G,\infty}$" is the glass transition temperature at a theoretical infinite molecular weight, "K" is an empirical parameter related to the "free volume" of the polymer sample that depends on the temperature and the number of polymer chain ends in the system. "M_n" is the molecular weight of the sample.

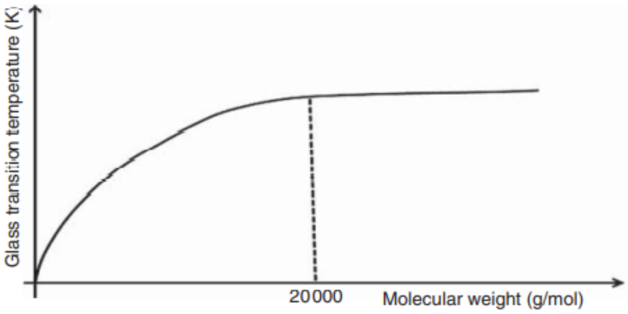


Figure 2-18: Variation of glass transition temperature with molecular weight of polymer [29]

Before moving to the specifics of the mechanical properties, it would be more appropriate to recap some fundamentals. The mechanical properties are directly related to the atomic bonds between the particles inside the material, which could be of different nature (covalent, ionic, VdW etc.). In general, this behaviour can be understood looking at the Condon-Morse curves (Figure 2-19) in which the attractive/repulsive force/energy between the particles are plotted in function of the interatomic distance.

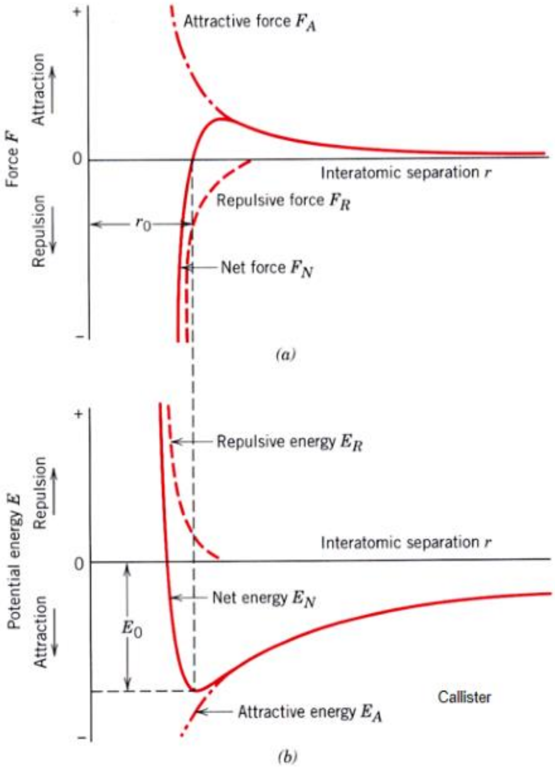


Figure 2-19: Condon-Morse curves [18]

The *Elastic modulus* “*E*” (Equation 2) is directly proportional to the tangent of each curve, evaluated at the equilibrium interatomic distance “r_0”, thus:

$$E \propto \left(\frac{dF}{dr}\right)_{r_0} \tag{2}$$

The easiest way to have a look at the behaviour of the materials undergoing to a certain load is to use the stress-strain curves (Figure 2-20) in which the overall mechanical characteristics are embodied. Those properties are function of various external factors, such as the temperature, chemical composition of the material and of the environment, strain-rate and so on.

The stress “σ” is basically the strength that the material can withstand before breaking, usually measured in $\frac{N}{mm^2}$ (referring to the cross-section area of the small specimens) and so in MPa. There are several types of strength, tensile (stretching), compressional, flexural (bending), torsional (twisting). The strain “ε” is intended as the elongation of the material starting from an initial value, measured in mm.

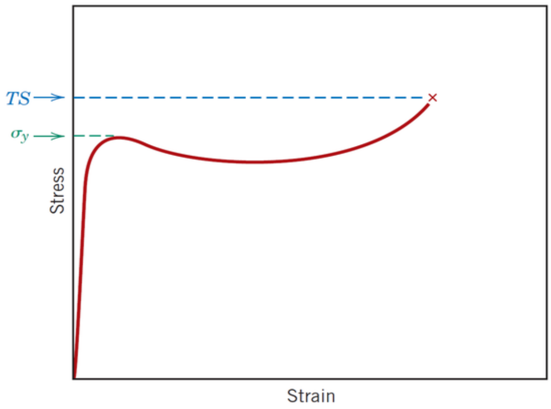


Figure 2-20: Generic stress-strain curve for a polymer [17]

In these curves the elastic modulus, aka *Young’s Modulus “E”*, is given by the ratio between the stress and the strain (Equation 3), and is a measure of the stiffness of the material:

$$E = \frac{\sigma}{\varepsilon}\ [Pa] \tag{3}$$

The toughness corresponds to the energy that the material can absorb before breaking and is measured as the area under a stress-strain curve (Equation 4):

$$Toughness = \int \sigma \, d\epsilon \tag{4}$$

Some factors are strictly linked to the strength of the polymers: the tensile strength increases with the molecular weight since for low MM the polymeric chains are tied together by means of weak (VdW) interactions, while for larger MM the polymers become bulky and entangled together producing high strength values. The relative motions of the chains are inhibited by the presence of cross-linked morphology, resulting in a strengthening of the material; the main parameter that affects the polymer strengthening is the degree of crystallinity, the more the crystalline regions the stronger the intermolecular bondings.

A brief and simplified overview of the behaviour of a generic polymer withstanding a certain load can be reported, with the help of the plots in Figure 2-21. The region in which the behaviour is linear is called "Elastic region" since no residual strain would occur, if the stress applied to the material is removed. The slope of the curve is constant and equal to the Young's Modulus. Around a certain stress value, the elastic region ends at the so called "yield strength" σ_y (see Figure 2-18, point B in Figure 2-21). Therefore, plastic deformations start to occur. After the yield strength, if the load is removed the material will remain deformed with a certain residual strain, the behaviour in the plot is a straight line that goes back with a constant slope. Otherwise, applying a continuous stress, the fibers start to strain and the bondings between the chains become weaker and weaker (this fact can be appreciated looking at the decreasing of the stress value with the increasing strain), a compression state will occur, and the polymeric chains start to align, leading to the necking phenomenon. Therefore, a sudden increase in the stress value occurs, resulting in the Tensile Strength "TS" (see Figure 2-18, point D in Figure 2-21), at which the failure of the material occurs.

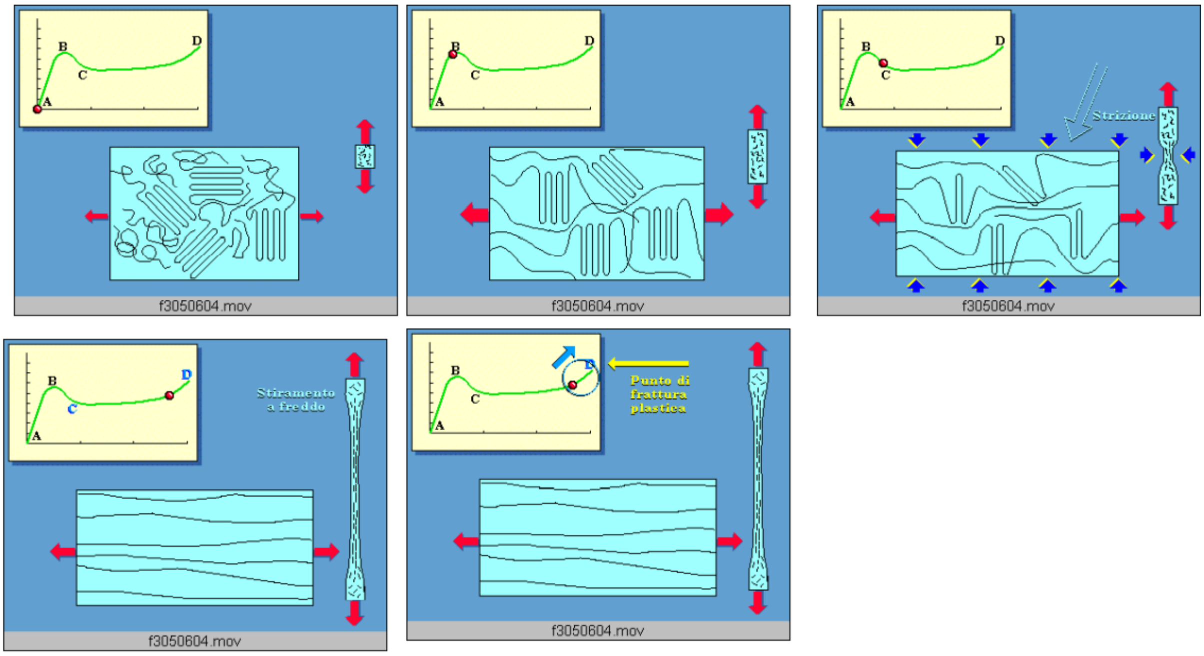


Figure 2-21: Plastic deformation of a semicrystalline polymer [17]

Different types of polymers can be distinguished in function of their structure and properties. Referring to the curves plotted in Figure 2-22, basically the polymers are classified in three categories: brittle, ductile and elastomers.

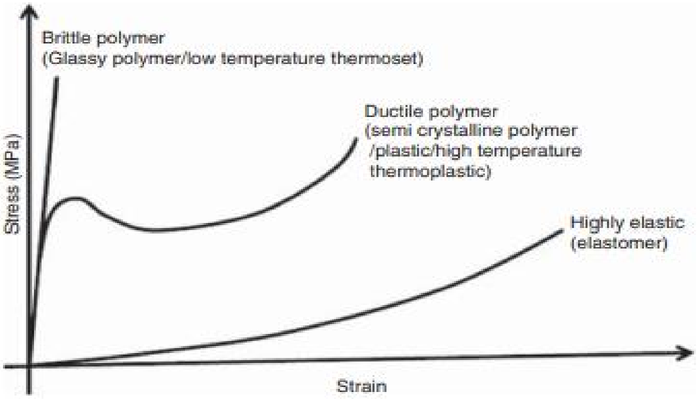


Figure 2-22: Stress-strain behaviour of different types of polymers [29]

Brittle polymers are characterized by high Young's modulus and are able to strain only in the elastic field (the yield strength coincides with the tensile strength), reaching the fracture much earlier if compared to the other classes of polymers. A characteristic of those materials is the failure surface, which is perpendicular to the load direction, rough and grainy (front decohesion).

However, due to the bulky constituents, rigid chains (as thermosets) and low cohesive forces, these types of materials have good adhesive strength, fracture toughness, tensile and compressive strength, and wear resistance. Some common examples are: "polystyrene, polyvinyl acetate, polylactic acid, polyvinyl chloride, polymethyl methacrylate, polysulfone, poly(ether sulfone), polyimide, polycarbonate, etc." [31].

Ductile polymers practically show properties as the ones explained above, characterized by a yield strength after which the material strains in the plastic field until it reaches the tensile strength. They can show very different behaviour, and this can be highlighted in Figure 2-23. They can be hard and strong with a high elastic modulus but not efficient in the plastic region, easily reaching the tensile strength. On the contrary, they could be soft and tough or maybe hard and tough, with good capability to strain in the plastic field but with different toughness value. "Examples of semi-crystalline polymers are linear polyethylene (PE), polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE) or isotactic polypropylene (PP)" [32]. Concerning the failure surface, in general it is smooth a skewed of 45° with respect to loading direction.

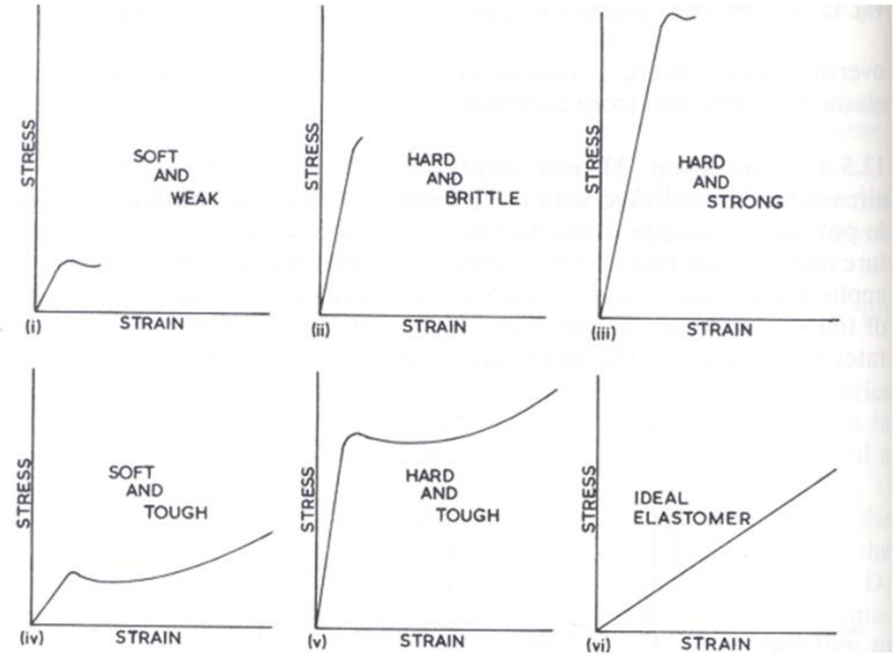


Figure 2-23: Types of stress-strain diagrams for different polymer group [17]

Before passing to the explanation of the other class of polymers, an important feature of the above-mentioned materials must be introduced, namely the ductile to brittle transition temperature (DBTT). It simply identifies, as it suggests, the temperature below which a ductile polymer becomes brittle. There is no common value of DBTT polymers but rather it is specific of every single one and this is a crucial parameter to be considered in the selection of the material during the failure analysis.

A specific standard to measure this temperature value has been stated and this is ISO 6603-2 [33](multi-axial instrumented impact), which determines the puncture impact properties of flat and rigid plastics. If the impact behaviour can be easily determined by a threshold value, the ISO 6603-1 can be applied [33]. As an example, Figure 2-24 can be used to clarify the idea. In this diagram the stress-strain curves of poly(methylmethacrylate) are plotted for different operative temperatures (in a completely normal range at our latitude). Starting from 60°C with a completely ductile behaviour, the temperature is progressively decreased, and the polymer becomes less tough until 4°C are reached and the behaviour results completely brittle. More specifically, the DBTT is strictly related to the degree of crystallinity of the polymer, since the presence of amorphous region establish different behaviour at different temperatures. In general, "Crystalline polymers show high strength & less ductility than the same polymers in the amorphous state at the same temperature" [34].

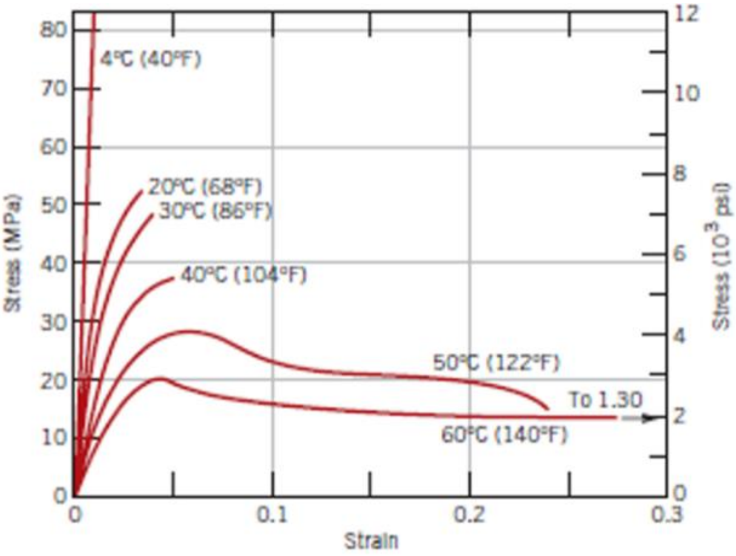


Figure 2-24: Influence of the temperature on the stress-strain characteristic of poly(methylmethacrylate) [17]

Lasts but not least, the elastomers are a particular type of polymers, highly elastic and rubbery. Thanks to their low Young's modulus, they are able to stretch a lot with high elongation at break. They are characterized by a DBTT well below the room temperature. Their molecular structure is composed of long chains, so long that can return easily to the original configuration without residual deformations when the stress is removed. Usually the term "elastomer" is confused with the term "rubber", since the latter refers to vulcanised rubber. The vulcanisation process consists in the hardening of the rubber by means of the introduction of sulphur bridge between the polymeric chains (Figure 2-25) that work as a cross-link.

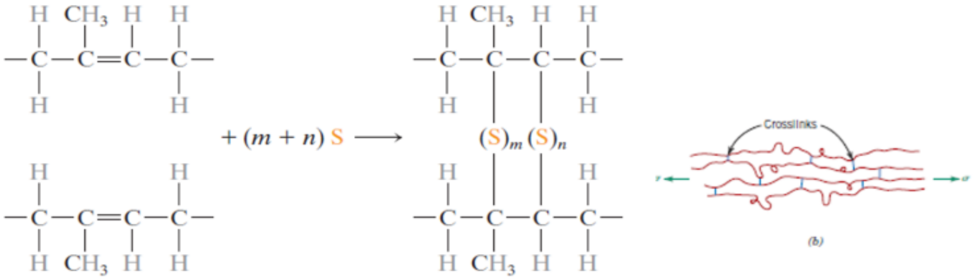


Figure 2-25: Introduction of sulphur bridge during vulcanisation of rubber [17]

Therefore, the toughness of the rubbers is increased as can be seen in the diagram of Figure 26. These polymers can be classified in three categories: diene, non-diene and thermoplastic elastomers, as shown in [35]. The first category is obtained through polymerisation of monomers with two sequential double bondings. Examples are polyisoprene, polybutadiene, and polychloroprene. Non-diene (such as butyl rubber (polyisobutylene), polysiloxanes (silicone rubber), polyurethane (spandex), and fluoro-elastomers, have no double bondings and should be obtained by means of condensation polymerisation or free radical polymerisation. The latter contains hard and soft repeating units, and when cooled down under the T_G starting from the molten phase, the hard blocks form stiff regions acting as physical cross-links for the elastomeric blocks. Examples are SIS and SBS block copolymers and certain urethanes.

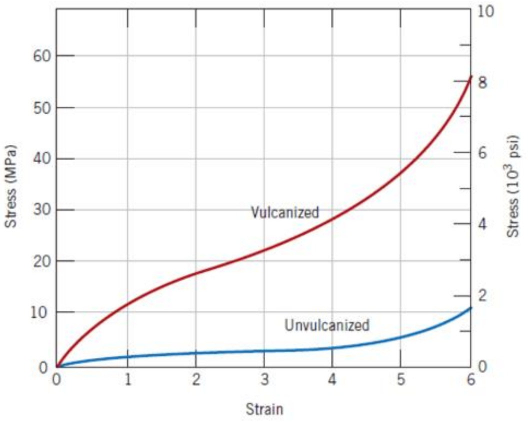
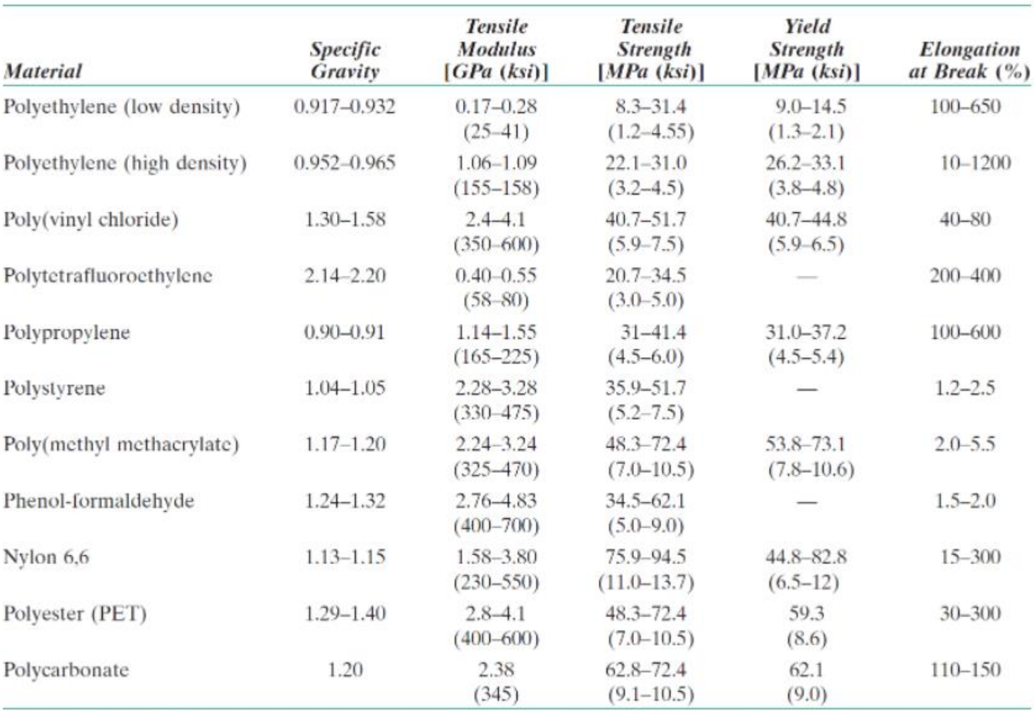


Figure 2-26: Stress-strain curves to 600% elongation for unvulcanised and vulcanised natural rubber [17]

Once the classes of polymers have been discussed, it would be useful to show some numbers for some properties of the more common polymers (Figure 2-27).



Material	*Specific Gravity*	*Tensile Modulus [GPa (ksi)]*	*Tensile Strength [MPa (ksi)]*	*Yield Strength [MPa (ksi)]*	*Elongation at Break (%)*
Polyethylene (low density)	0.917–0.932	0.17–0.28 (25–41)	8.3–31.4 (1.2–4.55)	9.0–14.5 (1.3–2.1)	100–650
Polyethylene (high density)	0.952–0.965	1.06–1.09 (155–158)	22.1–31.0 (3.2–4.5)	26.2–33.1 (3.8–4.8)	10–1200
Poly(vinyl chloride)	1.30–1.58	2.4–4.1 (350–600)	40.7–51.7 (5.9–7.5)	40.7–44.8 (5.9–6.5)	40–80
Polytetrafluoroethylene	2.14–2.20	0.40–0.55 (58–80)	20.7–34.5 (3.0–5.0)	—	200–400
Polypropylene	0.90–0.91	1.14–1.55 (165–225)	31–41.4 (4.5–6.0)	31.0–37.2 (4.5–5.4)	100–600
Polystyrene	1.04–1.05	2.28–3.28 (330–475)	35.9–51.7 (5.2–7.5)	—	1.2–2.5
Poly(methyl methacrylate)	1.17–1.20	2.24–3.24 (325–470)	48.3–72.4 (7.0–10.5)	53.8–73.1 (7.8–10.6)	2.0–5.5
Phenol-formaldehyde	1.24–1.32	2.76–4.83 (400–700)	34.5–62.1 (5.0–9.0)	—	1.5–2.0
Nylon 6,6	1.13–1.15	1.58–3.80 (230–550)	75.9–94.5 (11.0–13.7)	44.8–82.8 (6.5–12)	15–300
Polyester (PET)	1.29–1.40	2.8–4.1 (400–600)	48.3–72.4 (7.0–10.5)	59.3 (8.6)	30–300
Polycarbonate	1.20	2.38 (345)	62.8–72.4 (9.1–10.5)	62.1 (9.0)	110–150

Figure 2-27: Room Temperature mechanical characteristics of some of the more common polymers [17]

3. Carbon Fibers

In the last fifty years, carbon fibers (Figure 3-1) have become a widespread material because of their excellent properties. CFs are high-performance material widely used as reinforcement in advanced polymer-matrix composites (CFRPs will be treated in the further paragraphs). They are characterized by several advantages that can be easily found in literature [18], [36] and [37]. To cite some of them: CFs have the highest specific modulus/strength among all the reinforcing materials, showing high stiffness and tensile strength. At very high temperatures, they are able to maintain their high tensile modulus and high strength, even if oxidation can always be a problem. CFs are characterized by high chemical resistance not being affected by moisture, solvents, acids and bases and they can be engineered achieving different properties in function of the desired physical characteristics.

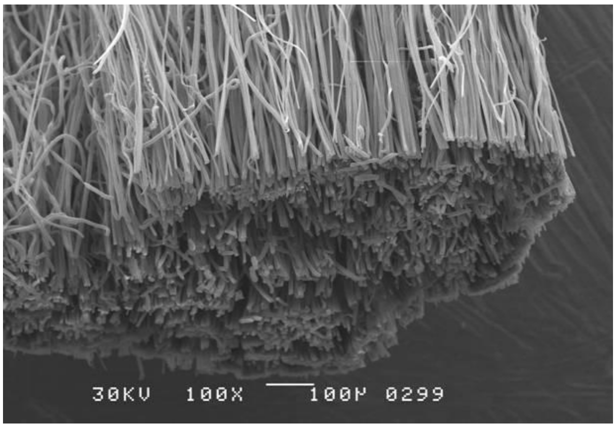


Figure 3-1: Carbon fibers at microscopic scale [38]

Thanks to these good properties, CFs have become very popular in different fields, being extensively used in sports, automotive field, pressure vessels and aircraft structural components (military and commercial). “In 2012, estimated global demand for carbon fiber market was $1.7 billion with estimated annual growth of 10–12% from 2012 to 2018” [37]. Nowadays, CFs are mostly sought-after in aircraft/aerospace field, wind turbines and the automotive field. At present, CFs capacity is estimated to be around 160 ktons (Table 3-1 extracted from [39] and rearranged).

Table 3-1: Carbon fibers producers and capacity [39]

MANUFACTURER	**COUNTRY**	**CAPACITY AT 2022 [kton]**
Toray (incl. Zoltek)	**Japan**	**55**
Hexcel	**USA**	**16**
Mitsubishi Chemical Carbon (Fiber & Composites)	**USA**	**16**
Teijin	**Japan**	**14**
SGL carbon	**Germany**	**13**
Formosa Plastics	**Taiwan**	**9**
Solvay (Cytec)	**USA**	**4,4**
DowAksa	**USA/Turkey**	**3**
Hyosung	**South Korea**	**2**
Various	**China**	**21,8**
Various	**Rest of the wolrd**	**5**
TOTAL		**≃ 160**

3.1 A brief hystory on carbon fibers

According to the paper mentioned in [39], CFs appeared for the first time, in 1860, as heated cotton fibers in an oxygen-free environment created by Joseph Wilson Swan, followed by Thomas Edison in 1879 who obtained CFs from the heating of cellulose. Later in 1958, Roger Bacon was able to grow carbon whiskers with exceptional mechanical properties, built as rolled-up sheets of graphite layers along all the whiskers length, achieving strength and elastic modulus in the order of 20 GPa and 700 GPa respectively. Some more information about the introduction of the CFs during the last decades can be found in [39].

3.2 Carbon Fibers' precursors

CFs' characteristics strictly depend on the manufacturing technique and mainly on their precursors. Lots of information are collected in papers, reviews and textbooks. Hence, three main organic precursors are used: rayon, polyacrylonitrile (PAN) (Figure 3-3) and petroleum pitch. Nowadays, it is known that the precursor is almost exclusively PAN (made via solution, suspension or polymerization process), on which 90% of the production is based. The remaining part is subdivided between pitch and rayon base technologies.

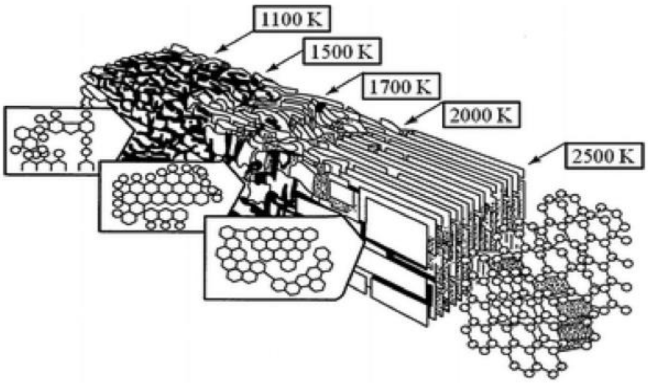


Figure 3-2: Structure development of a carbon fiber during carbonization and graphitization [39]

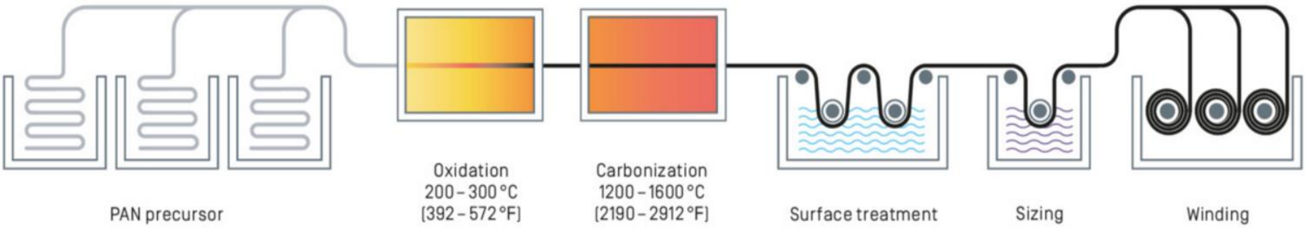


Figure 3-3: Schematic of the production chain of CF from PAN precursor [40]

Besides that, a lot of attention is given to alternative precursors such as lignin, cellulose or polyethylene, in order to significantly decrease the production cost. However, since the CF manufacturing techniques are relatively complex and are not included in the focus of this report, further information can be found in [39], [41]and [42].

3.3 Properties and structure of carbon fibers

A brief overview of the structure and physical properties of the CFs is reported in this chapter. Starting from the structure of these fibers, their diameter lies in the range 4÷10 μm [18] and can be found both in chopped and continuous form (Figure 3-4).

(a) (b)

Figure 3-4: Continuous (a) and chopped (b) carbon fibers [43]

Moreover, the atomic structure is similar to that of graphite, compose of graphene sheets (carbon atom layers) disposed in a hexagonal pattern. These layers can be turbostratic, graphitic or a hybrid structure, depending on the precursor and on the manufacturing processes. As it has been said in the previous chapter, this argument is not contemplated in this report, but additional information about atomic structure, treatments for each precursor and properties are available in cited literature and papers.

In general, the high crystallinity leads to high modulus values. Therefore, carbon fibers are classified in different types and in function of their modulus and tensile strength (Table 3-2).

Table 3-2: Types of carbon fibers in function of E and TS [36]

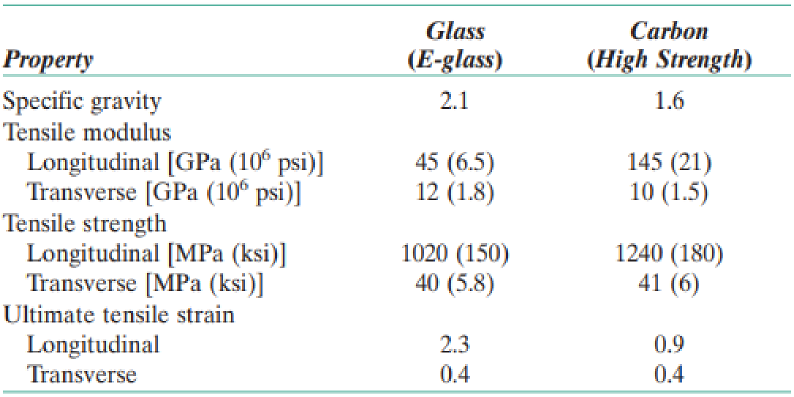
Ultra-high modulus(UHM)	E >450 GPa
High modulus (HM)	E = 350 ÷ 450 GPa
Intermediate modulus (IM)	E = 250 ÷ 350 GPa
Low modulus and High Tensile (HT)	E < 100 GPa and TS > 3 GPa
Super-high tensile (SHT)	TS > 4.5 GPa

Another distinction can be based on the final heat treatment temperature [36] (Table 3-3):

Table 3-3: Types of carbon fibers in function of final heat treatment temperature [36]

Type I	high-heat-treatment carbon fibers (HTT), where final heat treatment temperature should be above 2000°C and can be associated with high-modulus type fiber
Type II	intermediate-heat-treatment carbon fibers (IHT), where final heat treatment temperature should be around or above 1500°C and can be associated with high-strength type fiber
Type III	low-heat-treatment carbon fibers, where final heat treatment temperatures not greater than 1000°C. These are low modulus and low strength materials

The significant diffusion of these fibers is due to their excellent physical properties, in particular their strength-to-weight ratio since they are strong and light. If compared to the commonly used glass fibers, much higher Young's modulus and tensile strength can be appreciated (Figure 3-5), which means that CFs are characterized by good stiffness and resistance.



Property	*Glass (E-glass)*	*Carbon (High Strength)*
Specific gravity	2.1	1.6
Tensile modulus		
Longitudinal [GPa (10^6 psi)]	45 (6.5)	145 (21)
Transverse [GPa (10^6 psi)]	12 (1.8)	10 (1.5)
Tensile strength		
Longitudinal [MPa (ksi)]	1020 (150)	1240 (180)
Transverse [MPa (ksi)]	40 (5.8)	41 (6)
Ultimate tensile strain		
Longitudinal	2.3	0.9
Transverse	0.4	0.4

Figure 3-5: Properties of continuous and aligned glass- and carbon-fibers reinforced epoxy matrix composites (fibers volume fraction at 60%) [1]

As reported in the above-mentioned literature for further information, at the end of the manufacturing process, the fibers are coated with polymers (usually epoxy resins) to prevent them from being damaged during the winding or weaving. Even if CFs are corrosion resistant and chemically stable, the polymer can deteriorate under chemical-, bio-, thermal- and light-degradation (other matrices different than polymers can also be reactive).

Carbon fibers are characterized by good resistance to fatigue load and good tensile strength. It should not be forgotten that CFs are brittle since the above-mentioned layers are characterized by strong covalent bonds and due to the sheet-like aggregation the cracks propagate very fast. Therefore, this brittle behaviour leads to:

- Sudden decrease of the modulus and catastrophically failure under fatigue failure.
- The failure at small strains when tested in tensile mode.

In the next chapter, particular attention is given to the mechanical properties of the CFs, in which CFRPs are discussed.

In order to add further information, the latest development in CFs consists in the "carbon nanotubes" that show superior properties (more can be found in [39]).

Furthermore, it is well known that the stronger the bonds, the less the crystalline lattice vibrate and vice versa. Hence, since CFs are characterized by strong bonds, at high temperatures the vibrations of the lattice are restrained, making CFs suitable for applications where small movements can be critical. Translating this fact into numbers, fibers have small and negative coefficient of linear thermal expansion (CLTE) in the range $-0{,}5 \sim -2{,}0 \cdot 10^{-6}\ K^{-1}$ in the fibers' axial direction [42].

As for the thermal properties, it is true that CFs have high crystallinity, but the change in the theme will worsen the phonons propagation. Therefore, the lattice can be engineered (i.e., aligning the graphene layers along the fiber axis), designing CFs for low or high thermal conductivity. To give an idea for the order of magnitude, their coefficient of thermal conductivity lies in the range $21 \sim 125 \ \frac{W}{mK}$ [42], close to that of metals.

Once the properties that set the CFs so widespread are introduced, a summary table (Table 3-4) with the various sector (and the relative properties of interest) is introduced.

Table 3-4: Application fields of CFs

FEATURE/PROPERTY	APPLICATION FIELD
Physical strength, specific toughness, light weight	Aerospace, automotive, marine transport, sports
High dimensional stability, low CTE, low abrasion	Missiles, aircraft brakes, aerospace antenna and support structure, large telescopes, optical benches, waveguide for high frequency measurement
Good vibration damping, strength and toughness	Audio equipment, loudspeakers for Hi-fi equipment, robot arms
Electrical conductivity	Automobile hoods, novel tooling, casings and bases for electronic equipment, EMI and RF shielding, brushes
Biological inertness and x-ray permeability	Medical applications in prostheses, surgery and x-ray equipment, implants
Fatigue resistance, self-lubrication, high damping	Textile machinery, general engineering
Chemical inertness, high corrosion resistance	Chemical industry, nuclear field, valves, seals and pump components in process plants
Electromagnetic properties	Large generator retaining rings, radiological equipment

4. Carbon Fiber Reinforced Polymers – CFRPs

Nowadays, in the structural field, the advanced materials are continuously researched, and the use of technological processes is growing rapidly. In specific fields, like in the engineering, the use of the common conventional materials (such as metals, polymers, ceramics, etc.) is not enough, since their application is limited by their properties (i.e., large monolithic pieces of metals cannot be used and sometimes materials with their same stiffness but lighter are needed). In order to face specific requirements, composites are introduced.

"A composite material is a heterogeneous material composed of two or more integrated constituents for enhanced structural performance" [17]. Most of the composites are composed of just two phases: the former is the matrix, which is continuous and involves the strengthening phase; the latter is the dispersed phase, which could be of different shapes, different nature and geometry (distribution, size and orientation). A simple schematic classification of composite materials is shown in Figure 4-1a.

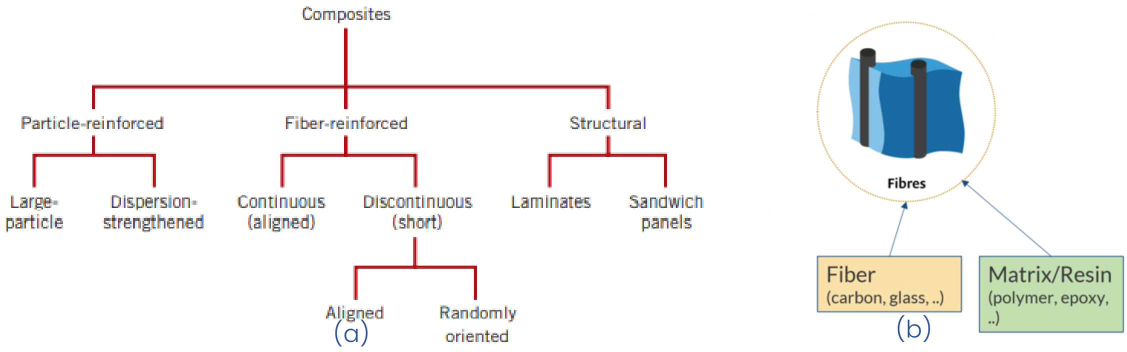


Figure 4-1: (a) classification scheme for the various composite types [18], (b) demonstration of a fiber reinforced polymers [17]

In broad terms, the dispersed phase for particle-reinforced composites is approximately equiaxed, for the fiber-reinforced ones has the geometry of a fiber with large length-to-diameter ratio, while for the structural ones are combinations of composites and homogeneous materials. Further insights can be found in [18], since the report is focused on the fibers reinforcement.

4.1 A brief overview on CFRPs

However, the strengthening material can be of different nature: polymeric, metallic or ceramic. The choice is performed in function of the required characteristics of the materials (e.g., for aerospace field, it is preferred to substitute precise metallic components with CFRPs for fuel-saving since they can show the same stiffness but with less weight). A clarifying scheme is shown in Figure 4-2, in which the specific strength of different materials is plotted in function of the operative temperatures.

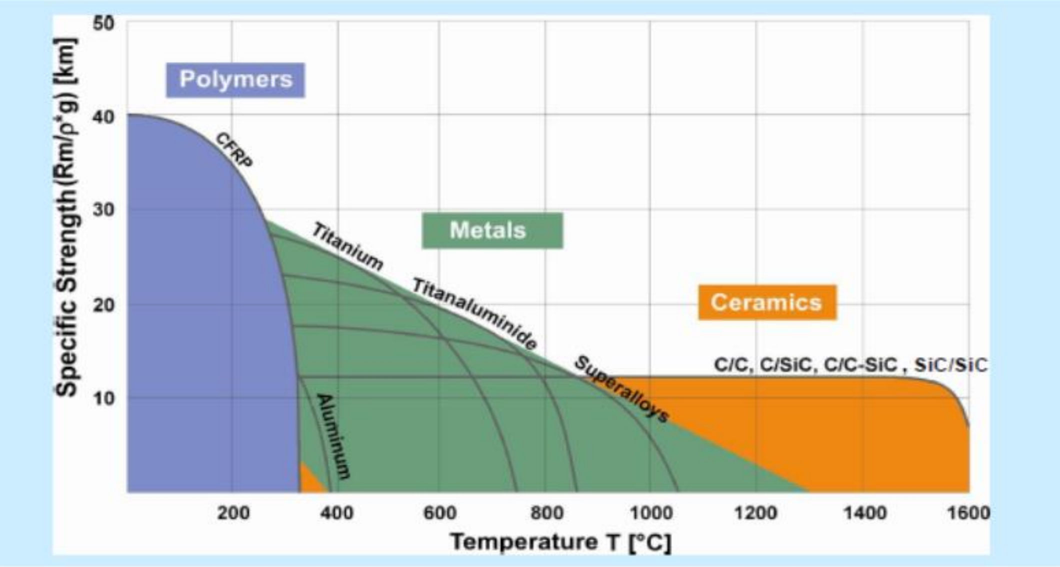


Figure 4-2: Mass specific strength vs. Temperature of structural materials [17]

As a first approximation, the rules of mixture can be applied to predict most of composite properties, such as the elastic modulus. Starting from the particle-reinforced composites, Equation 5 can be applied, with reference to the volume fraction of the two constituents:

$$E_c = E_m f_m + E_p f_p \tag{5}$$

In the case of the fiber-reinforced composites, the moduli for continuous and aligned fibrous composite both in the longitudinal direction and in the transverse direction are given by Equation 6 and Equation 7 respectively:

$$E_{cl} = E_m f_m + E_f f_f \tag{6}$$

$$E_{ct} = \frac{E_m E_f}{E_m f_f + E_f f_m} \tag{7}$$

At least, the one for the discontinuous and randomly oriented fiber-composites is evaluated by means of Equation 8:

$$E_{cd} = E_m f_m + K E_f f_f \tag{8}$$

In which “K” is a fiber efficiency parameter, function of the ratio between the moduli of the fibers and of the matrix, its magnitude is lower than 1 (in most of the cases comprised between 0.1 and 0.6). Note that the rule of mixture can be applied also in the evaluation of density, thermal/electrical conductivity.

In this report the properties of the fiber-reinforced composites with a polymeric matrix are treated, since the focus are the CFRPs. Further information on the other types of reinforcing materials can be found in [18].

Nowadays, as it is cited in [18], the most important composites are the fibers-reinforced ones, characterized by exceptionally high specific strengths and moduli, with low-density fiber and matrix materials (see the previous chapter on polymers). As depicted in Figure 4-3, they can be of different nature, but the Carbon Fibers are one of the best choices, because of the properties showed in the previous chapter that make them suitable for high-performance applications.

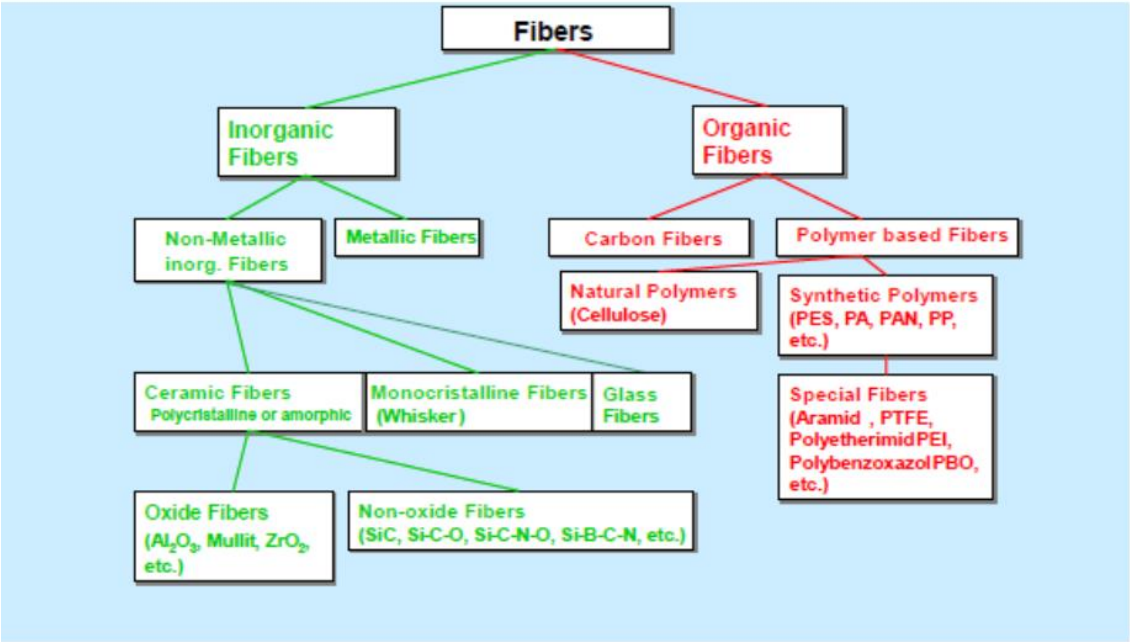


Figure 4-3: Classification of fiber-reinforcing materials [17]

4.2 Mechanical properties of CFRPs

Previously the composites were introduced as materials composed of two constituents: the matrix and the dispersed phase. In reality, a third player should be introduced, which is the interface between the matrix and the fibers. FRPs require a strong interface (one of the reasons why the CFs are preferred) so that the load from the fibers (brittle materials) can be transferred to the matrix (non-brittle material). A clear representation can be found in Figure 4-4.

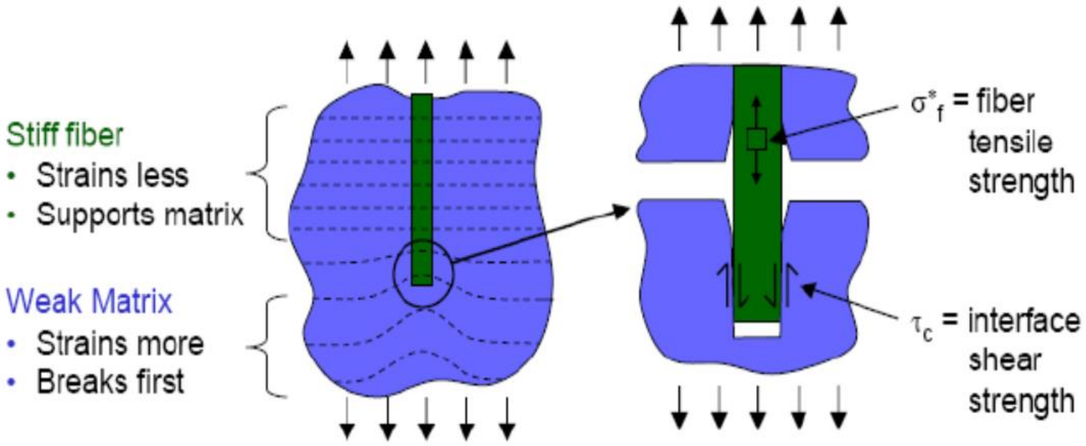


Figure 4-4: Schematic of the interactions between fibers and interface [17]

Another important parameter is the critical length of the fibers, on which the load transferred from the fibers to the matrix is strictly related, more information in [18]. Furthermore, a stress vs. strain behaviour can be analysed by means of the schematic in Figure 4-5, considering brittle fibers (such as CFs) and the matrix phase to be reasonably ductile (like a polymer).

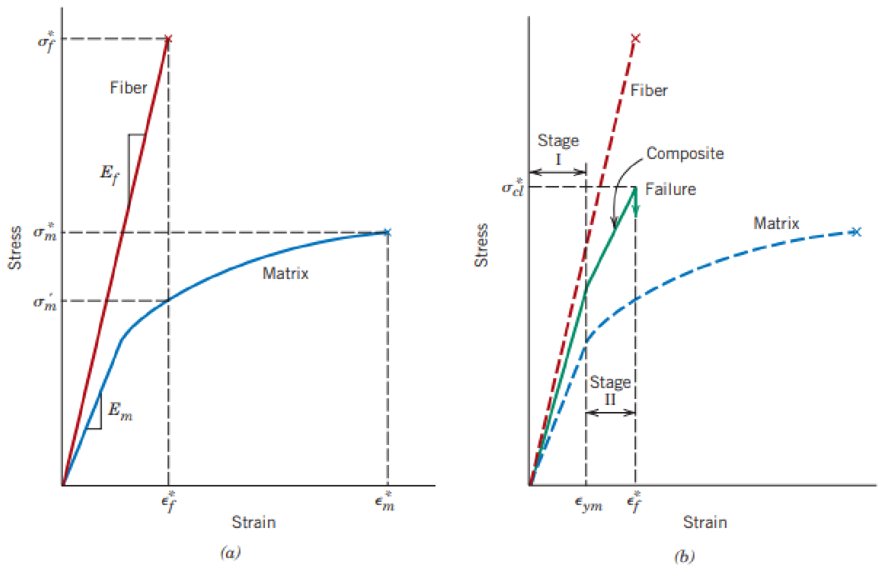


Figure 4-5: (a) Schematic stress–strain curves for brittle fiber and ductile matrix materials. Fracture stresses and strains for both materials are noted. (b) Schematic stress–strain curve for an aligned fiber-reinforced composite that is exposed to a uniaxial stress applied in the direction of alignment; curves for the fiber and matrix materials shown in part (a) are also superimposed [18]

The different behaviours between fibers and matrix can be appreciated in Figure 4-5a, useful just to give a perspective. Otherwise, looking at the Figure 4-5b, a CFRP-like composite behaviour is highlighted, in which the materials show the uniaxial stress-strain response. In the initial “Stage I”, both materials strain in the elastic field and the resultant elastic modulus is given by Equation 6. Hence, in the “Stage II”, the polymeric matrix starts to deform plastically, while the fibers continue to strain linearly. Since the matrix now contributes little to the stiffness, the portion of the modulus related to the matrix in Equation 6 can be considered negligible, and the composite’s modulus is dependent on the fibers contribution. In fact, as can be seen in Figure 4-5b, in the “Stage 2” the slope of the composite decrease once the matrix contribution is lost. Then the fracture of the fibers starts to occur, but it won’t lead to a catastrophic failure of the composite, since not all the fibers fracture at the same time. A schematic of this mechanism is represented in Figure 4-7. Nevertheless, once a fiber is broken, it will always be embedded within the matrix, being capable of contributing to the load withstanding as the matrix continues to deform in the plastic field, and so on even if the fibers are fractured and divided in small pieces. This is true until they are pulled out from the matrix (e.g., Figure 4-6), the stronger the interface, the higher the energy required to pull-out the fibers. This mechanism is called “pull-out and debonding” and it is one of the most effective mechanical energy consuming mechanisms known in nature (more insights can be found in [44]).

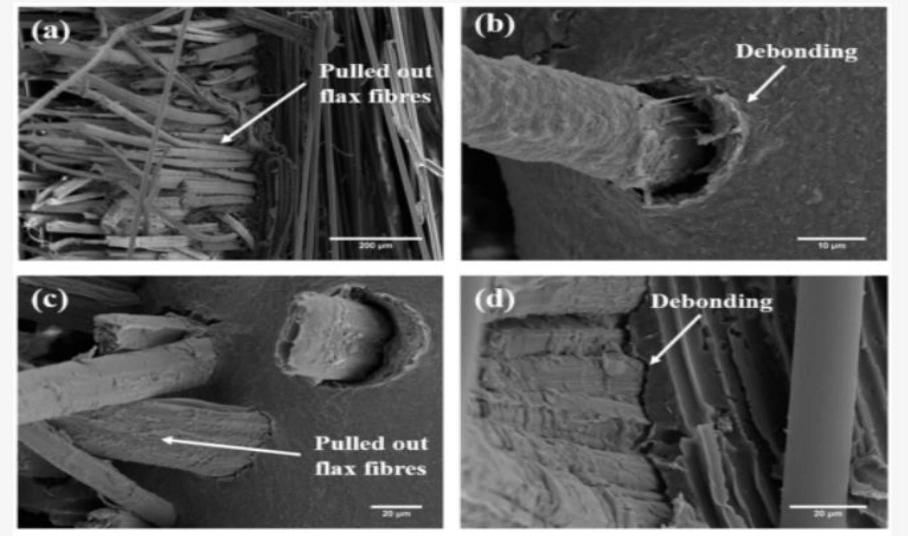
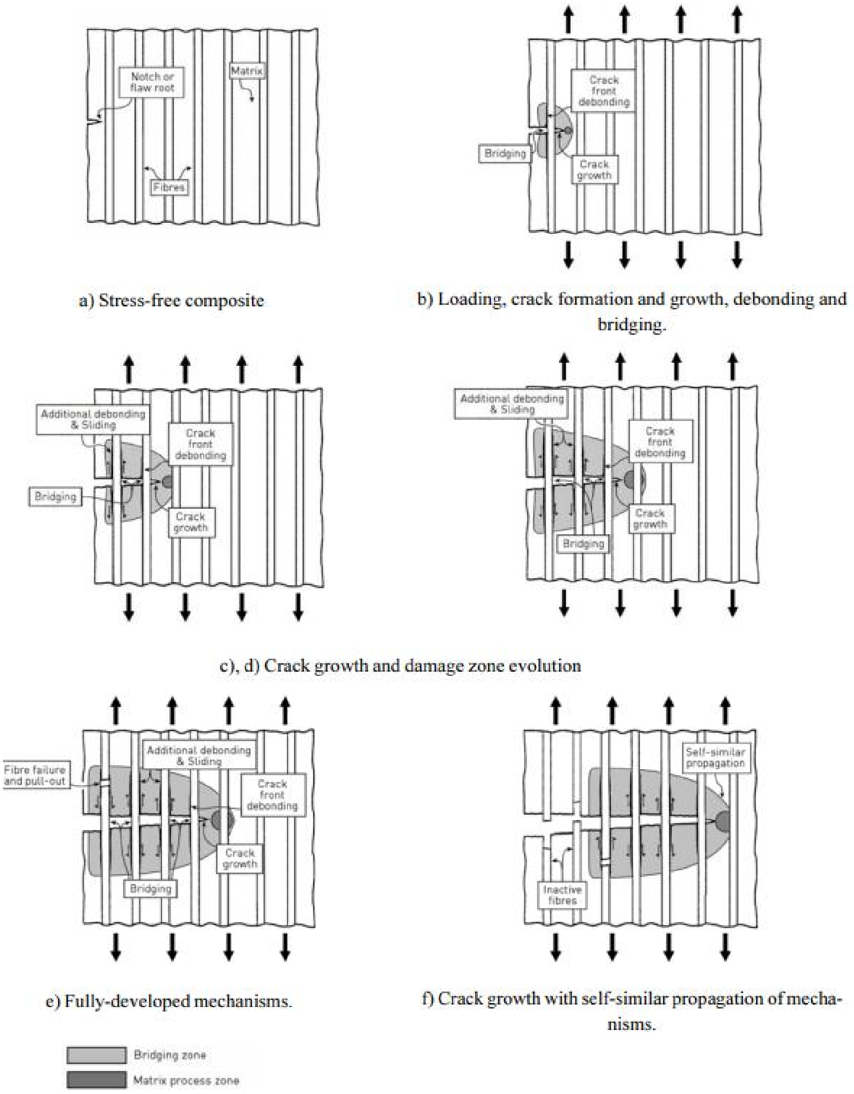


Figure 4-6: - SEM micrographs of failed flexural H_PP specimens at different magnifications, highlighting the presence of extensive fiber pull-out and debonding [45]



a) Stress-free composite

b) Loading, crack formation and growth, debonding and bridging.

c), d) Crack growth and damage zone evolution

e) Fully-developed mechanisms.

f) Crack growth with self-similar propagation of mechanisms.

Figure 4-7: Consecutive phases in the fracture sequence of a continuous fiber-reinforced composite (qualitative, not-to-scale diagram) [44]

Another important aspect is related to the fibers' orientation, which have a significant influence on the load that the composite can withstand. The material in question is highly anisotropic, which means that its properties are strictly related to the direction in which they are measured. Hence, the maximum strength that the material can withstand is obtained in the direction parallel to the fiber displacement. On the contrary, the load in the direction perpendicular to the fiber, the withstanded load is negligible (Figure 4-9). According to the fiber displacement, two configurations are possible:

- Parallel alignment of the longitudinal axis of the fibers, continuous or discontinuous (Figure 4-8a and 4-8b respectively).
- Totally random alignment (Figure 4-8c).

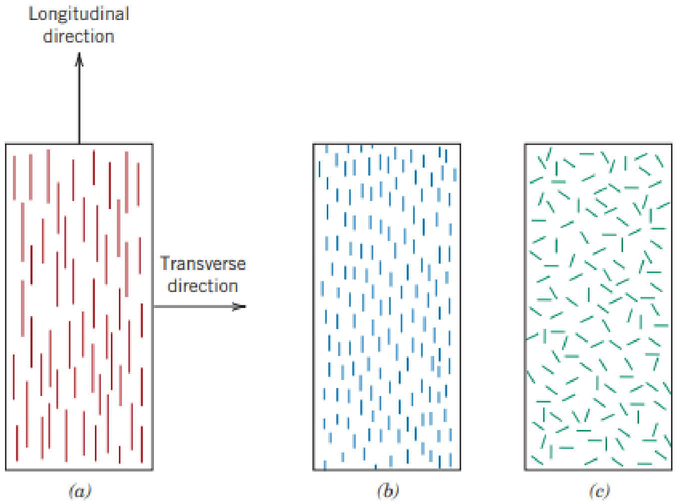


Figure 4-8: Schematic representations of (a) continuous and aligned, (b) discontinuous and aligned, and (c) discontinuous and randomly oriented fiberreinforced composites [18]

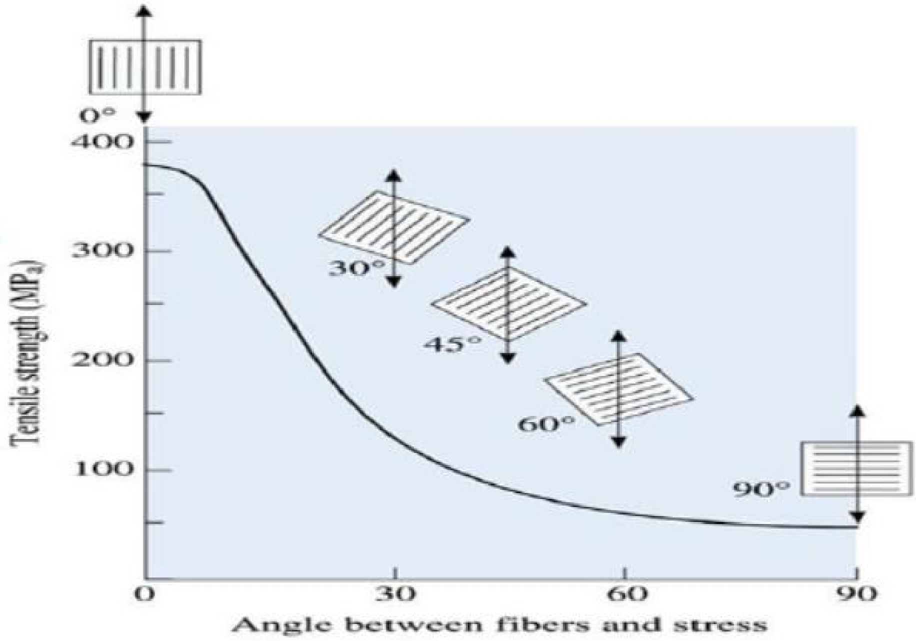


Figure 4-9: Graph of load vs. fibers' orientation [17]

Obviously, better properties can be obtained when the fibers are uniformly distributed. However, those materials can be upgraded, reaching quasi-isotropic configuration, displacing the fibers on different piles with different angulation (Figure 4-10), so that high loads can be applied on different directions.

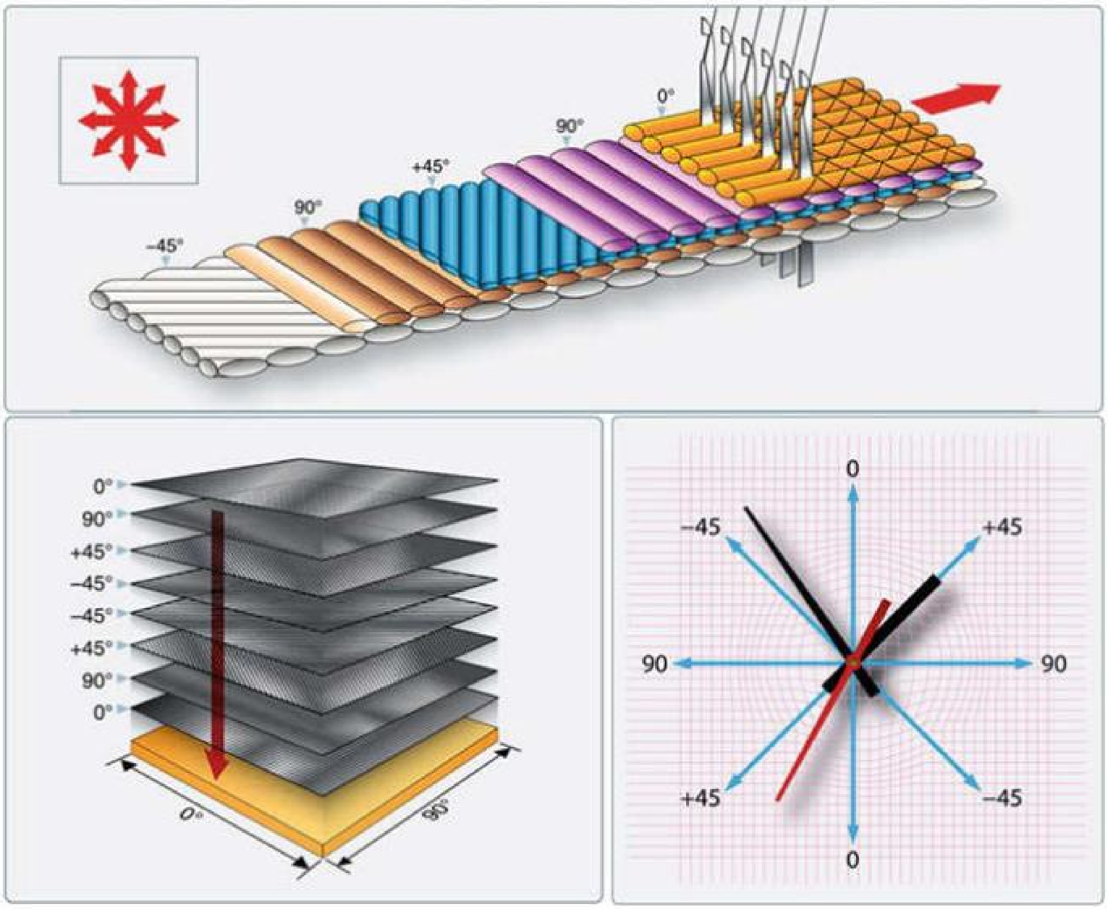


Figure 4-10: Illustration of fiber orientation angles format [46]

The properties of the CFRPs lead to various advantages (according to [46]), such as high tensile strength/modulus to weight ratio, practically negligible coefficient of thermal expansion, high fatigue strengths and thermal conductivity, specific strength up to 4500 MPa, stiffness with damping feature. Unfortunately, they also show some disadvantages, like the high cost and the high electrical conductivity, low breaking elongation and impact resistance. Nevertheless, these properties make them suitable for different applications such as aerospace automotive, electronics, medical and sport equipment components. A full section dedicated to the applications of CFRPs in aircrafts can be found in [46], which contains examples of applied CFRPs.

4.3 Production processes for CFRPs

As for the production of CFRPs, different methods can be applied in function of the polymeric matrix, which could be thermoset or thermoplastic. In this section the main manufacturing processes are discussed:

- Pultrusion - used to design components with a constant cross-sectional shape (such as tubes, beams, etc.); the fibers are initially drowned into a resin and then undergo to the machinery that give the desired shape (Figure 4-11). This process can be automated and can reach high production rates, it is very cost effective.

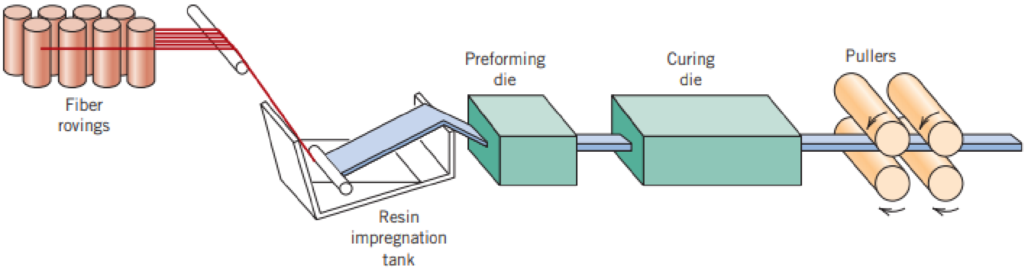


Figure 4-11: Schematic diagram showing the pultrusion process [18]

- Prepreg - "the composite industry's term for continuous fiber reinforcement pre-impregnated with a polymer resin that is only partially cured" [18]. Initially, a series of spooled fibers are collimated and sandwiched together by means of pre-impregnated sheets, with a process called "calendaring" (Figure 4-12), then the final product is collected by winding onto a cardboard core.

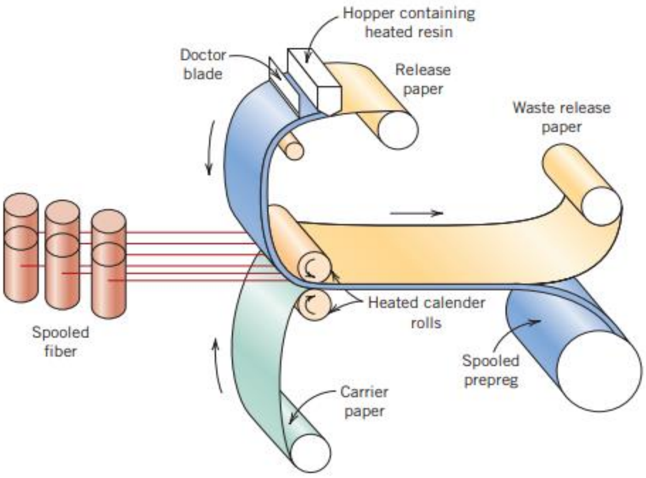


Figure 4-12: Schematic diagram illustrating the production of prepreg tape using a thermoset polymer [18]

- Filament winding - “is a process by which continuous reinforcing fibers are accurately positioned in a predetermined pattern to form a hollow (usually cylindrical) shape” [18]. In this case, the fibers are drowned into a resin bath and then wounded onto a mandrel by means of automated machinery. Various patterns can be obtained (Figure 4-13) with the desired mechanical properties.

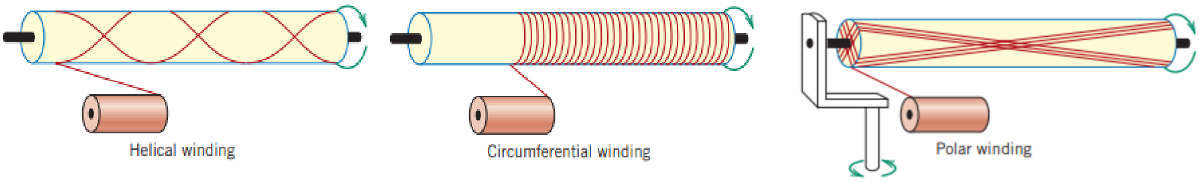


Figure 4-13: Schematic representations of helical, circumferential, and polar filament winding techniques [18]

5. Carbon Fibers recovery

In the previous chapters, the superior characteristics of the CFRPs were highlighted, analysing broadly both carbon fibers and polymeric matrix properties. A large variety of papers can be found in the e-journals, which contain a lot of information concerning the treated topic, with useful examples, figures and real applications. These can be found in the cited papers [47]- [70]. The different qualities that classify the Carbon Fiber-Reinforced Polymer composites as advanced materials lead them to be widely used within the last decades. Therefore, the application of CFRPs has been extended from aerospace sector to automotive industry, sporting goods, renewable energy and construction. As far as figures are concerned, the worldwide use of CFRPs was expected to be approximately 199 kilotons by this year [47], and in 2020, 3000 tons per year of waste were expected only in Europe and in the U.S. [48]. As an example, in [48] is reported that around 8500 commercial airplanes will be dismantled by 2025, being composed of 50% in weight by CFRPs. Nevertheless, the amount of these non-biodegradable wastes will exceed 263 kilotons by 2030 [49]. It seems clear that such a high demand introduces disadvantages, increasing the amount of CFRPs waste in the coming years. Currently, unsatisfactory solutions are adopted for the CFRPs disposal, being landfilled or incinerated, leading to serious environmental pollution. In the EU, the organization that encourage at reducing the amount of waste disposed and incinerated, promoting the recycling of these materials, is the European Union's Waste Framework [51].

Figure 5-1: Composites life cycle [57]

Obviously, the author in [52], which is a very interesting publication rich in useful information, states that the recycling process should be efficient, eco-friendly and cost-effective, highlighting three different methodologies to treat the waste: disposal (landfilling), energy recovery from steam (incineration) and recycling. Starting from the cheapest and most common, landfilling is definitely not an eco-friendly strategy to manage disposal so that both the EU and the US authorities put it under restrictive legislations, and obviously this method does not allow the energy recovery from the material ("disposing of CFRP by landfilling, where not illegal, can cost approximately 0.20 £/kg" [50]). For this purpose, incineration is used to partially release the embodied energy of the entire CFRP, releasing a huge amount of pollutant, such as GHGs, into the environment. Last but not least, the recycling method is the most challenging but continuously under innovative investigation, because it allows the recovery of the r-CFs from v-CFs (Figure 5-1).

It must be remembered that recycling is expected to be a less energy-intensive process with lower environmental impact than the traditional way to produce v-CFs. "Carbon fibre manufacturing is an energy intensive process (183–286 MJ/kg of carbon fibre), which transforms the precursors with poorly ordered structure into a nearly perfect graphite structure in carbon fiber (CF) and generates environment and human health impacts due to emissions from the oxidation and carbonization furnaces, such as HCN, NH_3, NO_X…" [58].

However, the application of the appropriate recycling technique strictly depends on whether the polymeric matrix is thermoplastic or thermoset. As explained in the previous chapter on polymers, the former group can be easily recycled, shaped and machined, while the materials of the latter group must undergo more complex processes because of their cross-linked and heterogeneous nature. In fact, "Thermoset matrices such as phenolic resins or epoxy resins cannot be re-processed, recycled, or altered into their monomeric state due to their 3D cross-linked structure" [52].

Thanks to the huge plethora of material available in literature and in various periodic, a lot of information were extracted, so that a classification of the different recycling methods and their pros and cons can be treated. As depicted in Figure 5-2, the main technologies aimed at recycling those type of materials are currently classified in three categories: primary, secondary and tertiary recycling technologies. However, each technique will be treated with more attention in the next paragraphs.

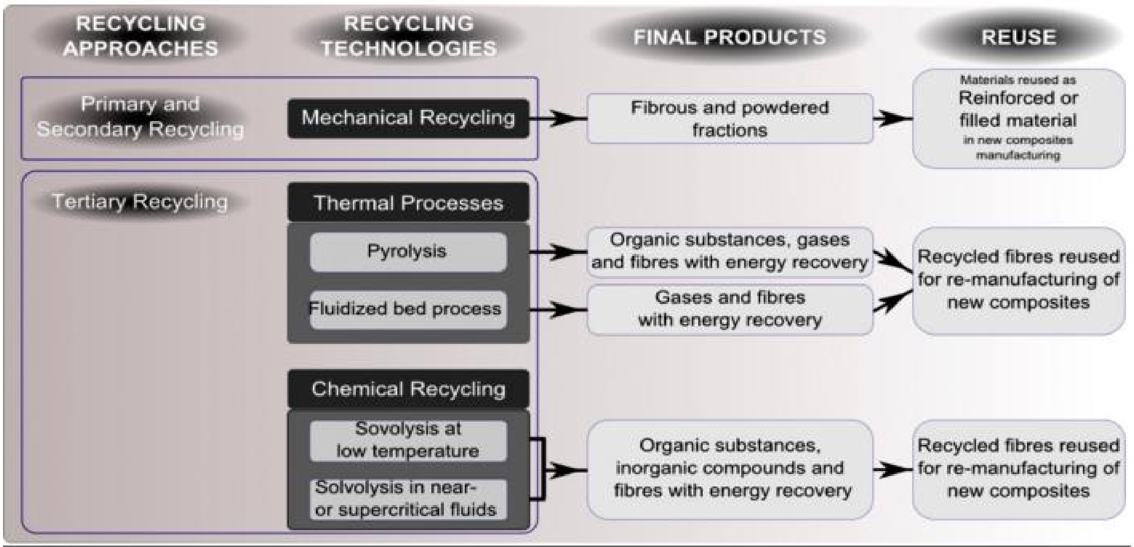


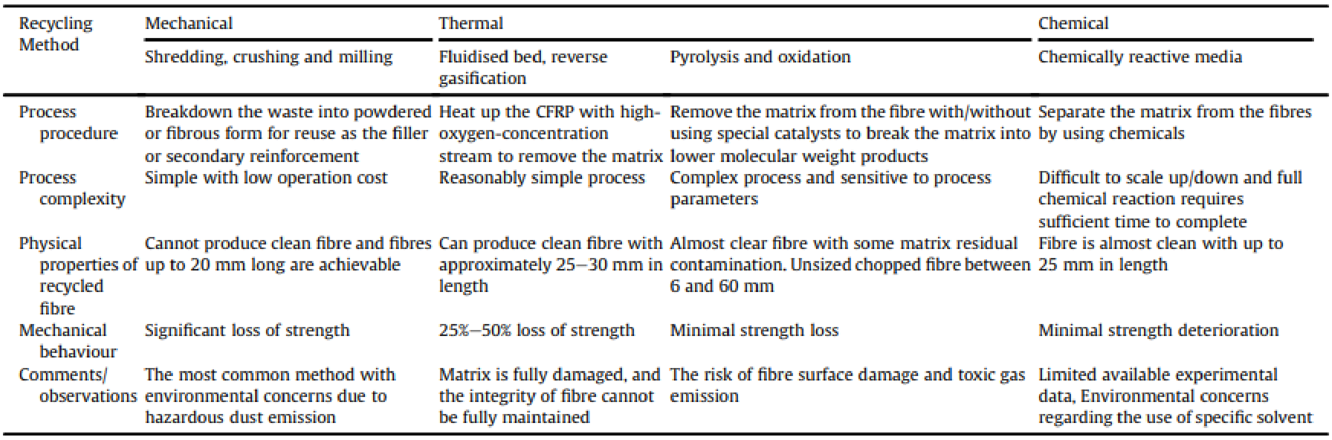
Figure 5-2: Recycling technologies for composite waste [53]

Primary and secondary recycling are better known as mechanical recycling, both based on crushing and milling the waste CFRP composites but deferred by the final properties of the recycled material compared to the virgin one: equivalent properties (primary), inferior properties (secondary). In the cases of CFRP composites, the CFs are recovered as powder or short fibres that can only be reused as fillers in the production of new composites.

Tertiary recycling techniques are based on the chemical decomposition of the polymeric matrix by means of thermal or chemical processes. In this case, CFs can be recovered with excellent properties so that they can be used as raw materials or mixed with virgin fibers. The thermal process consists in decomposing the polymer that covers the CF at high temperature (using pyrolysis or fluidized bed process), whereas chemical process consists of using solvents in function of the specific resin to be separated (solvolysis processes). Some examples can be found in the cited paper, such as [48] in which monoethanolamine – MEA is used to dissolve the polymer, or [54] in which nitric acid is used.

Not to be forgotten, there are alternative techniques like electrically driven catalytic decomposition. More information about the mentioned methods can be found in [55] and [56]. However, the key characteristics of the main recycling methods are summed up in Table 5-1, extracted from [49].

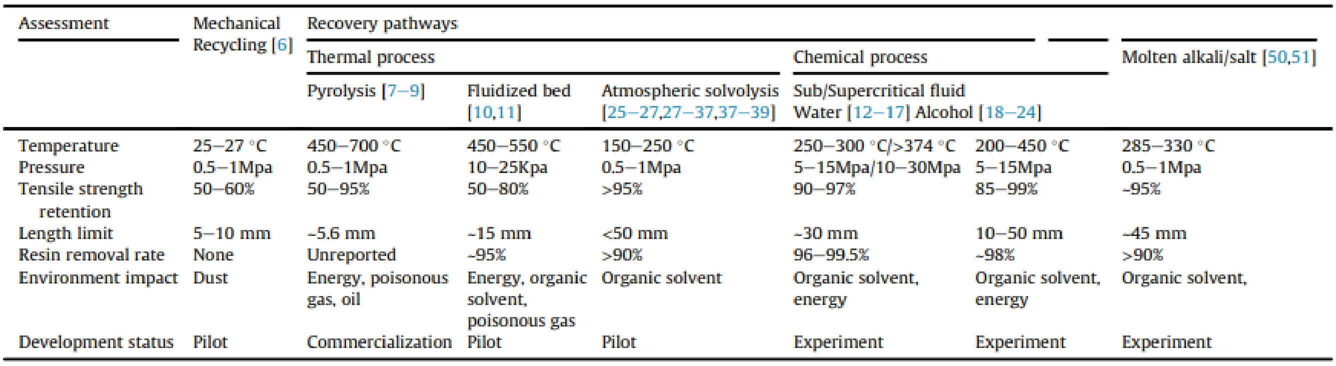
Table 5-1: Existing methods for carbon fibre reclamation from CFRP waste [49]



Recycling Method	Mechanical	Thermal		Chemical
	Shredding, crushing and milling	Fluidised bed, reverse gasification	Pyrolysis and oxidation	Chemically reactive media
Process procedure	Breakdown the waste into powdered or fibrous form for reuse as the filler or secondary reinforcement	Heat up the CFRP with high-oxygen-concentration stream to remove the matrix	Remove the matrix from the fibre with/without using special catalysts to break the matrix into lower molecular weight products	Separate the matrix from the fibres by using chemicals
Process complexity	Simple with low operation cost	Reasonably simple process	Complex process and sensitive to process parameters	Difficult to scale up/down and full chemical reaction requires sufficient time to complete
Physical properties of recycled fibre	Cannot produce clean fibre and fibres up to 20 mm long are achievable	Can produce clean fibre with approximately 25–30 mm in length	Almost clear fibre with some matrix residual contamination. Unsized chopped fibre between 6 and 60 mm	Fibre is almost clean with up to 25 mm in length
Mechanical behaviour	Significant loss of strength	25%–50% loss of strength	Minimal strength loss	Minimal strength deterioration
Comments/ observations	The most common method with environmental concerns due to hazardous dust emission	Matrix is fully damaged, and the integrity of fibre cannot be fully maintained	The risk of fibre surface damage and toxic gas emission	Limited available experimental data, Environmental concerns regarding the use of specific solvent

In addition, as it is said in [48], "the existing technologies are subjected to several shortcomings, such as stringent conditions, expensive reaction equipment, and damaged mechanical properties of carbon fibers" and this can be better understood by looking at Table 5-2, extracted from [48].

Table 5-2: Comparison of different recycling technologies nowadays [48]



Assessment	Mechanical Recycling [6]	Recovery pathways					
		Thermal process			Chemical process		Molten alkali/salt [50,51]
		Pyrolysis [7–9]	Fluidized bed [10,11]	Atmospheric solvolysis [25–27,27–37,37–39]	Sub/Supercritical fluid Water [12–17]	Alcohol [18–24]	
Temperature	25–27 °C	450–700 °C	450–550 °C	150–250 °C	250–300 °C/>374 °C	200–450 °C	285–330 °C
Pressure	0.5–1Mpa	0.5–1Mpa	10–25Kpa	0.5–1Mpa	5–15Mpa/10–30Mpa	5–15Mpa	0.5–1Mpa
Tensile strength retention	50–60%	50–95%	50–80%	>95%	90–97%	85–99%	~95%
Length limit	5–10 mm	~5.6 mm	~15 mm	<50 mm	~30 mm	10–50 mm	~45 mm
Resin removal rate	None	Unreported	~95%	>90%	96–99.5%	~98%	>90%
Environment impact	Dust	Energy, poisonous gas, oil	Energy, organic solvent, poisonous gas	Organic solvent	Organic solvent, energy	Organic solvent, energy	Organic solvent,
Development status	Pilot	Commercialization	Pilot	Pilot	Experiment	Experiment	Experiment

In the next paragraphs each technique will be properly discussed, so that a general overview can be appreciated. Then, a Life Cycle Assessment (LCA) will be discussed in order to underline the impact of each process on the environment.

5.1 Mechanical recycling

Thanks to the above-mentioned collected literature, the recycling technique based on mechanical processes can be fully understood (Figure 5-3). For the realisation of this report, several research in papers are used. Recycling of CF composites through mechanical methods has been under study. At the downstream of the process, the mechanically recycled composites are typically used as fillers or reinforcement in new composites (e.g., as fillers for artificial woods or asphalt, or as mineral sources for cement [50]). However, these are low-value applications and, due to this, most of the research in literature is focused on the recycling of the glass fibres from GFRPs. Nevertheless, applications to thermoplastic and thermoset CFRPs can be appreciated as well in paper such as [52], [57] in which some examples are cited and treated.

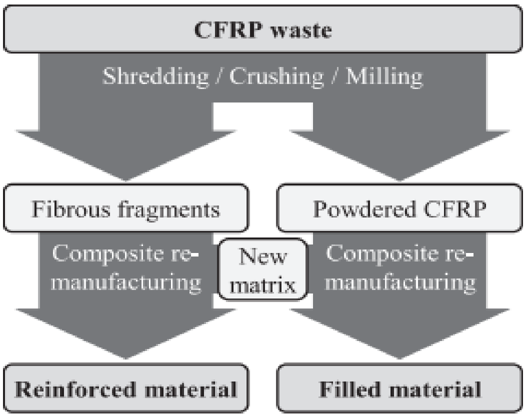


Figure 5-3: Mechanical recycling [4]

Mechanical recycling represents the easiest way to re-manufacture a composite material and is a practical way to manage the increasingly large volumes of CF waste, which are recycled without changing their initial structure. The process starts from the identification of the polymer matrix to be treated, remembering that the thermoplastic polymers can be easily remoulded and machined (e.g., polyethylene, polypropylene, etc.) an infinite number of times, instead of the thermoset polymers. The latter group of materials are the most used in mechanical recycling since they are cross-linked and cannot be machined and easily melted. Thus, it is possible to grind them up and to realise new low-value composites.

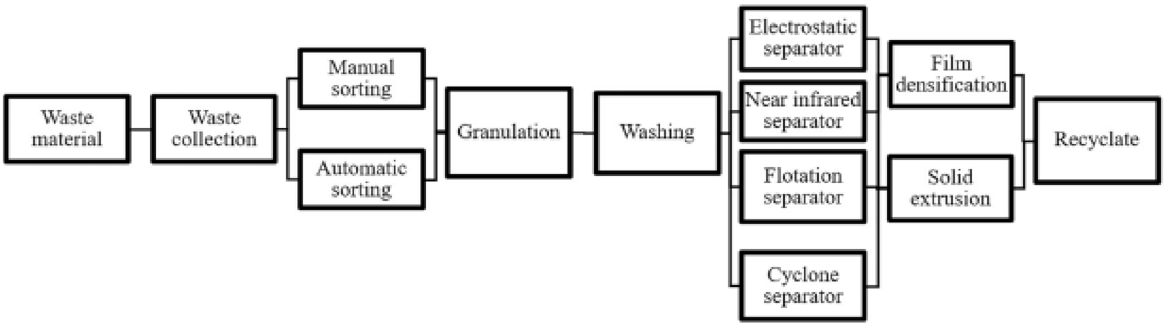


Figure 5-4: Flow diagram of mechanical recycling of the waste FRP [57]

This recycling process is based on a sequence of operations like sorting, cutting, shredding, crushing, rotary cutter, milling, separation techniques etc. (Figure 5-4). First of all, large pieces of waste CFRPs are sorted manually or automatically and then are granulated by means of shredding or cutting mills (Figure 5-5). The dimension and the uniformity of the produced pieces are a function of the distance between the blades, the sieve size and the rotation speed of the blades. Usually, the supplied waste composite is fed into "50-100 mm" [53] in size and then granulated in finer pieces "from 10 mm down to 50 μm in size" [53], taking into account that the decrease in size goes hand in hand with an increase of the energy consumption.

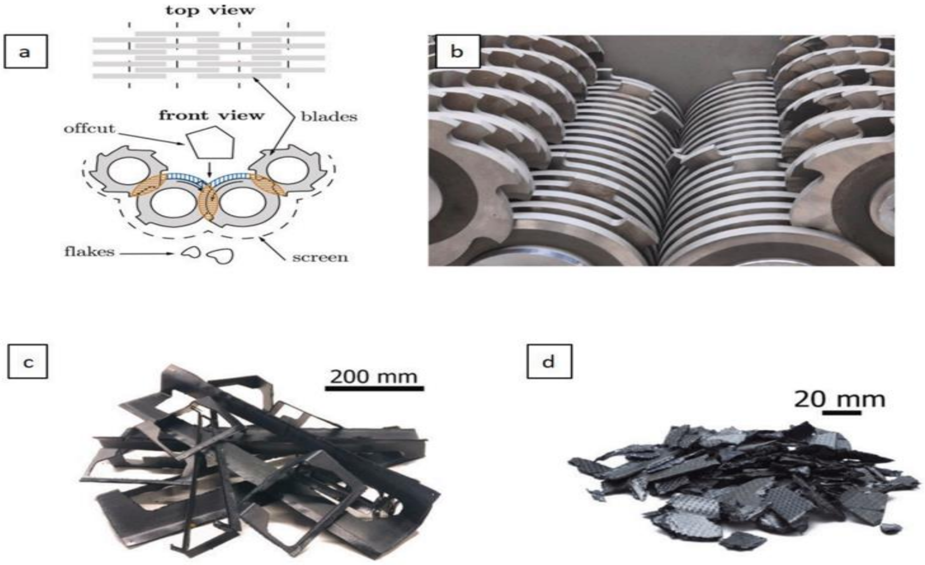


Figure 5-5: (a) Schematic illustration of top and front, and (b) inside views of a multiple-shaft shredding machine; CF/PPS offcuts (c) before and (d) after shredding [52]

Once the original components have been processed, the outcomes are sent to whatever separator that must be suitable for large particles. Examples are cyclones, sieves or electrostatic separator (Figure 5-4). Therefore, the different fractions of the composite are separated by size: coarse or fine particles. The former group represents the fibrous fraction (reused for reinforcing purposes), while the latter is referred to the powdered fraction composed mainly by the polymeric matrix (reused as active fillers or in sheet moulding compound composites). This process leads to a few advantages as it permits to recover both matrix and fibers, without pollutant production. Nevertheless, the mechanical properties are degraded because of the unstructured architectures, coarse and non-consistent. As a consequence of that, the re-manufacturing applications are limited. In general, as it is reported in [53], if a thermoset composite is filled with 50% of recovered fibrous fraction and mixed with v-CFs, the mechanical properties remain unaltered. Otherwise, if filled with 100% of recycled parts, mechanical properties are degraded.

Thanks to the collected literature, some properties of the r-CF can be discussed, accompanied by a little research. This is the case of "Colucci et al." [52] that have investigated the effects of the mechanical recyclability upon mechanical properties of PA66 (polyamide 66) filled with short CF.

They have found that the reduction of the elastic modulus and of the tensile strength is strictly related to the ageing of the matrix and that the shortening of the CFs after the recycling process has negligible impact on the mechanical properties. The experiment was realised imposing an artificial ageing process by means of a proper UV-irradiation. Then, the aged composite underwent a recycling process (Figure 5-6). At the end, it is clear that the photo/thermo-oxidative degradation of the polymeric matrix is the main responsible of the reduction in mechanical properties.

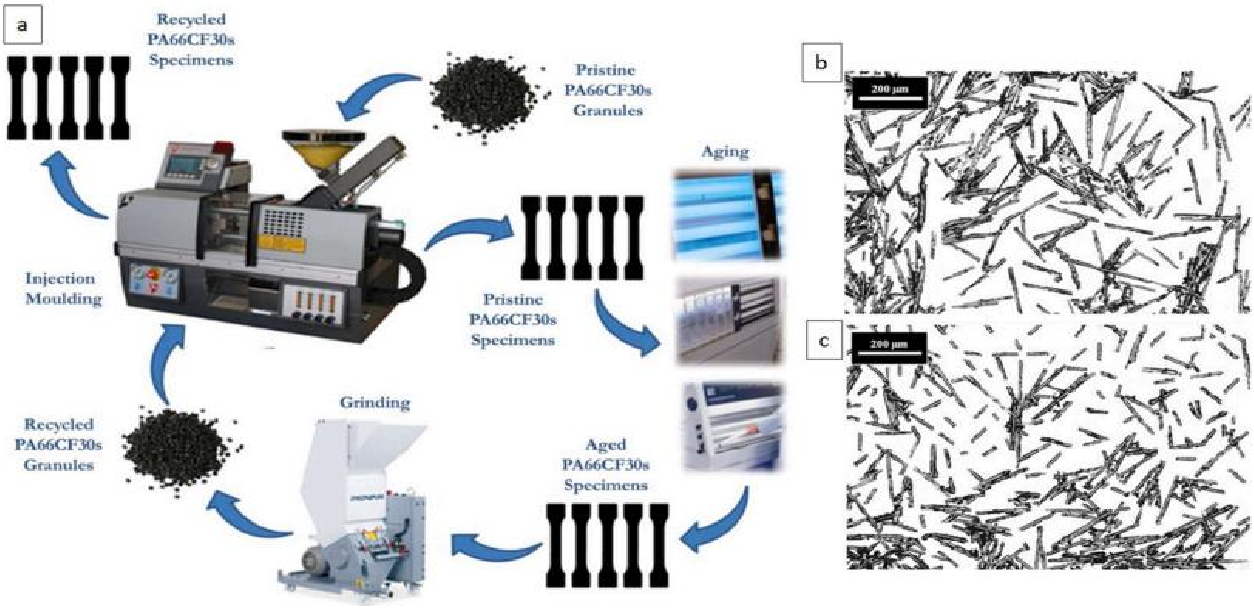


Figure 5-6: (a) the production procedures of PA66/CF composites and their mechanical recycling; optical images of CF (b) before and (c) after recycling process by "Colucci et al." [52]

Furthermore, the dependence of the r-CFs quality and of the energy consumption on the clearances between the machine blades, the thickness of the fed composites and the sieves mesh size, has been demonstrated by “Shuaib and Mativenga” [52]. Other studies were performed mixing r-CFs with concrete or reincorporating them into thermoplastic resins, obtaining different values of tensile modulus/strength that increase with the increasing percentage in weigth of r-CFs (see [57]). Some of the most recent studies are reported in [52], [57].

5.2 Pyrolysis process

Compared to the other recycling methods, pyrolysis technique is still progressing at industrial level and some research is focused on improving the efficiency of the process (discussed in the following lines). Before introducing the process for the recycling of the CFRP composites waste, some fundamentals have to be recalled. "Pyrolysis can be defined as the decomposition of a molecule by high temperature within a nonreactive atmosphere" [59]. In our case the pyrolysis process is referred to the thermal decomposition of the polymeric matrix in almost absence of oxygen (inside an inert atmosphere filled with N_2 or Ar), with controlled pressure and temperature (Figure 5-7). The properties of the r-CFs, in fact, strictly depend on some key parameters, such as temperature, residence time and reaction atmosphere components, even if the results are always inferior compared to the one of the v-CFs. As stated in [52], in general the temperature is controlled at more than 350°C and at atmospheric pressure.

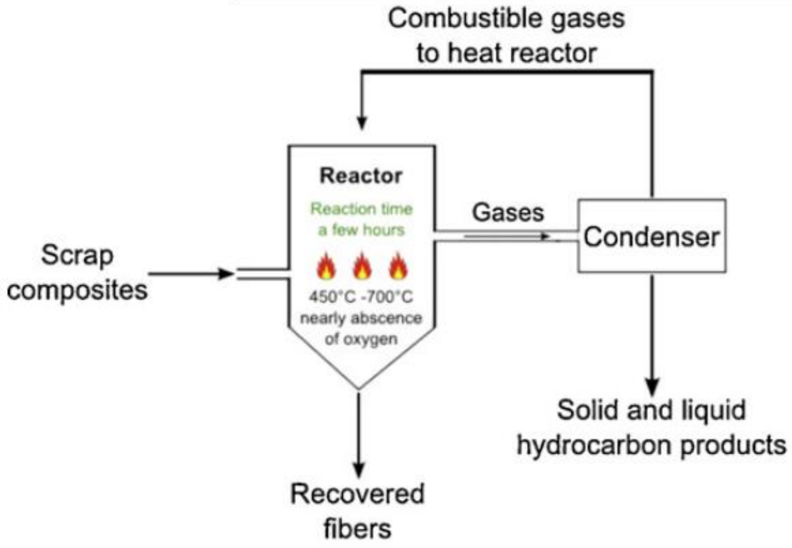


Figure 5-7: Schematic of pyrolysis process for the recycling of CFRPs [53]

In addition, the characteristics of the r-CFs are not as good as the ones of the v-CFs (crystallinity, sizing, impurities etc.) and may contain some resin residues. If carbon fibers manufacturing requires 183÷286 MJ/kg , this process requires around 10÷50% [52] of the energy consumption required for the v-CF production. The breaking down of the matrix not only produces recycled fibers and fillers, but also co-products such as solid and oily products characterised by lower molecular weight (e.g., polyaromatic chars, benzene, toluene, ethyl benzene and phenols), and gaseous products (H_2, CH_4, CO and CO_2). Thanks to the high calorific value, the oily and the gaseous co-products can be stored and re-used as fuel or secondary source. A post-pyrolysis oxidation step could be introduced to eliminate the pyrolytic char layer on the fibers surface after the pyrolysis process, even if the pyrolytic chars play a tricky role that will be fully understood in the following lines. As a result, the r-CFs are suitable for non-structural applications (automotive, industry, sports equipment etc.) since cannot be considered a perfect substitute for the v-CFs.

The processing parameters were investigated, since their optimisation can lead to better efficiencies and to properties of the r-CFs closer to the one of the v-CFs (e.g., strength retention up to 90%). Thanks to the abundant literature, some research of the past was found, in which pyrolysis process at different temperatures and operating conditions were investigated. The first company able to perform a continuous pyrolysis recycling line, aimed at producing commercial recycle CFs, was "Recycled Carbon Fibre Ltd. (RCF)" [53], UK in 2008. However, Ushikoshi et al. [57] applied different operative temperatures (400 °C, 500 °C and 600 °C) in an inert atmosphere, discovering that the r-CFs contained good mechanical properties with a superficial morphology comparable with the one of the original fibers. Furthermore, Meyer et al. [53] investigated parameters such as variation in temperature, isothermal dwell time and nitrogen and synthetic atmosphere, by means of thermogravimetric analysis (TGA). Their research has shown that the decomposition in nitrogen atmosphere is temperature dependant, while in synthetic air atmosphere it is more time and temperature dependant (see [53] for more info). Another important research was developed by "Nahil and William" [52] (2011), in which they pyrolyzed a CFRP (made of woven carbon fibres and polybenzoxazine resin) in a static bed reactor (depicted in Figure 5-8) at 350, 400, 450, 500 and 700 °C for 1 h with a heating rate of 5 °C/min, with a successive post-oxidation carried at 500 and 700 °C. The best results were obtained with a pyrolysis and oxidation temperature of 500 °C, reaching the 93% and 96% of the tensile strength and Young's modulus respectively. For what concerns the char layer on the fibers, the higher the oxidating temperature, the lower the time required for their elimination. With an oxidating temperature of 500 °C, the chars were eliminated in 2 h instead of the 15 min required for 700 °C, but in despite of the short dwell time the mechanical properties were deteriorated (with only 36% retention of the tensile strength). Nahil and Williams also discovered that the solid, liquid and gaseous yields are strictly dependant on the polymer matrix and the operating temperature.

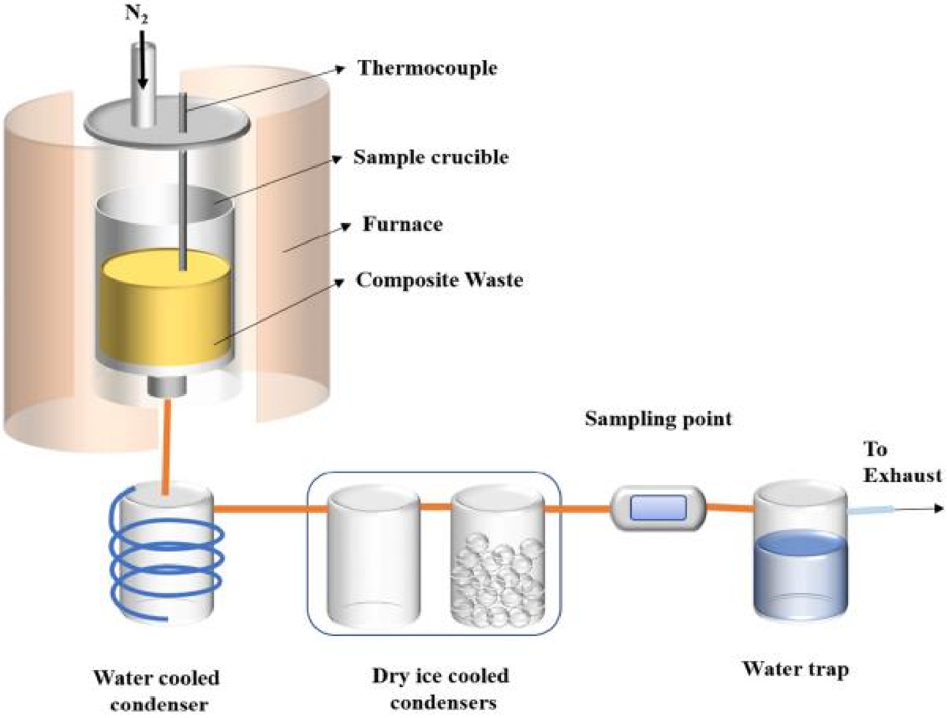
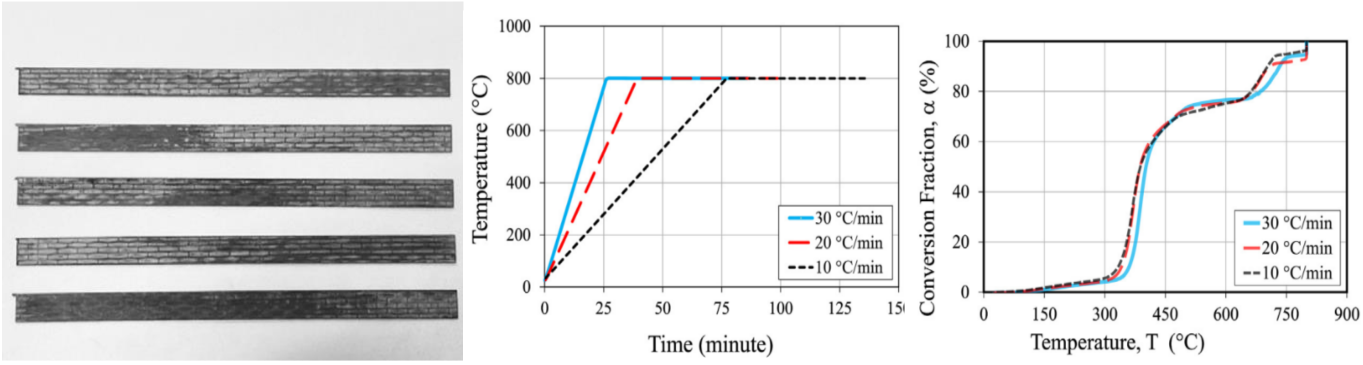


Figure 5-8: Static bed pyrolysis reactor [52]

In 2018, Mazzocchetti et al. [52] studied the effect of the oxidation time and the damage level imposed on the fibers, highlighting the tricky role of the pyrolytic char layer. He performed the research comparing the effect of oxidation on both v-CFs and pyrolyzed CFs. Starting from the v-CFs, applying oxidation at 500 °C for 1 h, the fibers degradation led to 10% diameter reduction. While for the pyrolyzed fibers 1 h was just enough to remove the char layer (which increases the fibers diameter by 10%). This pyrolytic layer acts as a scapegoat, avoiding the reaction of oxygen with C atoms and reducing the overall damage to the fibers. Thus, acting on the pyrolysis and oxidation parameters permits to optimize the retention of fibers mechanical properties of the r-CFs.

Mazzocchetti et al. have shown that CFs can be oxidized at 600 °C with no dwell time or at 500 °C with 120 min dwell time [48]. He also noticed that epoxy composites with v-CFs and r-CFs can exhibit similar mechanical properties. This is possible due to the enrichment of the pyrolyzed fibers with oxidized groups, after the oxidation process, which act as cross-linkers between r-CFs and new resin. The studies in the above-mentioned papers showed that pyrolysis can lead to products with high mechanical properties after the recycling process (with a strength retention up to 90%), if optimised parameters setting is used. Furthermore, one of the most recent researches (in 2021), carried out by "Hadigheh et al." [48] is focused on the achievement of an energy efficient and cost-effective pyrolysis, also improving the surface characteristics of the r-CFs. Hence, they investigated the kinetic behaviour of the composite thermal degradation, in order to optimise the key parameters, evaluating the activation energies on the basis of five different kinetic model that, for sake of simplicity, won't be treated in this report (see [48] for more info). Using composite coupons (Figure 5-9a) made of epoxy resin and 45% of CFs, they found that the pyrolysis process (in an inert atmosphere filled with nitrogen) can be divided in two stages, where 55% of the resin is removed during the first one. As a first try, the CFRPs coupons are heated up to 800°C in the first stage trying different heating rate, while in the second one the temperature is maintained for 60 min (Figure 5-9b and Figure 5-9c).



(a) (b) (c)

Figure 5-9: (a) CFRP composite samples, (b) variation of temperature during time for different heating rates, (c) average conversion fraction at different sample temperatures for different heating rates [48]

The surface morphology of the treated CFs can be monitored via Scanning Electron Microscopy (SEM), clear examples are reported in the following pictures. Nevertheless, also trying with different operative parameters settings, almost clean fibers were obtained (Figure 5-11a, b, c) but showing damaged surface (Figure 5-10c) or small amount of residual matrix/char (Figure 5-10d), even at 60 min dwelling time.

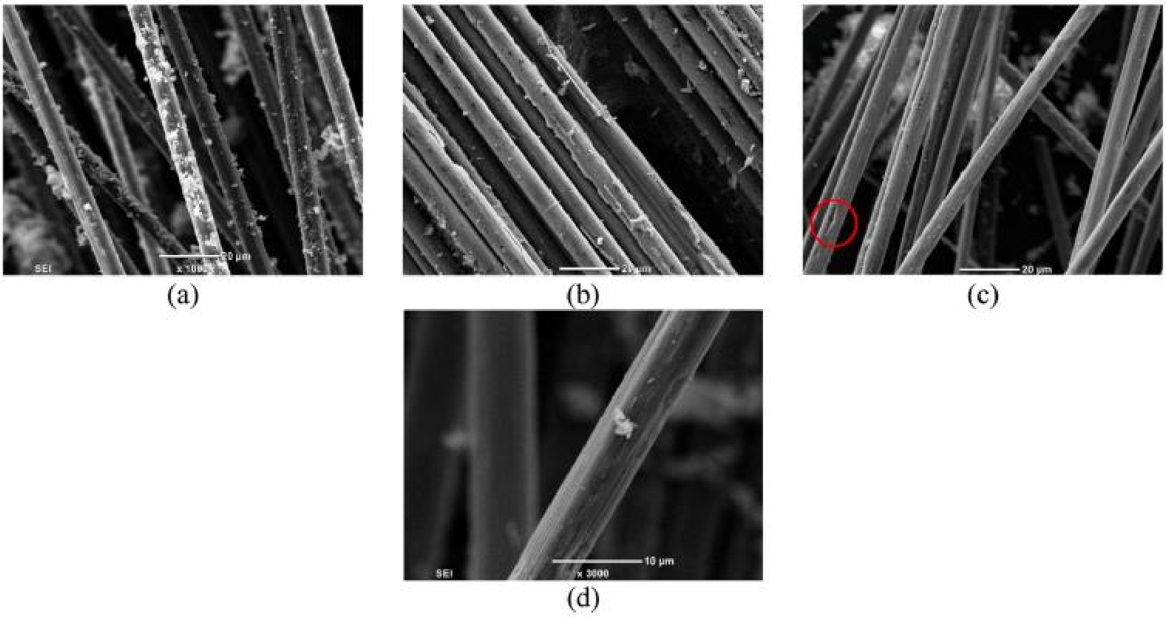


Figure 5-10: SEM images of reclaimed CF pyrolyzed up to (a) 425 °C with 60 min isothermal dwelling and (b) 680 °C with no isothermal dwelling, (c) 800 °C plus 30 min isothermal dwelling (heating rate = 20 °C/min), and (d) 800 °C with 30 °C/min heating rate and 60 min isothermal dwelling [48]

Thus, studying the kinetic behaviour (which is fully explained in [48]) the optimum values of the process were found. During the first stage, the energy input could be minimised since higher conversion rate can be achieved with lower heating rate. Therefore, the decomposition of the resin was efficient at 425 °C, but only stage one was not sufficient to produce high quality fibers. Therefore, stage two presented some issues since it was unstable and ineffective in the matrix removal. In fact, an oxidation step was introduced with temperature up to 550 °C and 10 °C/min. High quality recycled fibers can be obtained with this optimum configuration (Figure 5-11d, e, f).

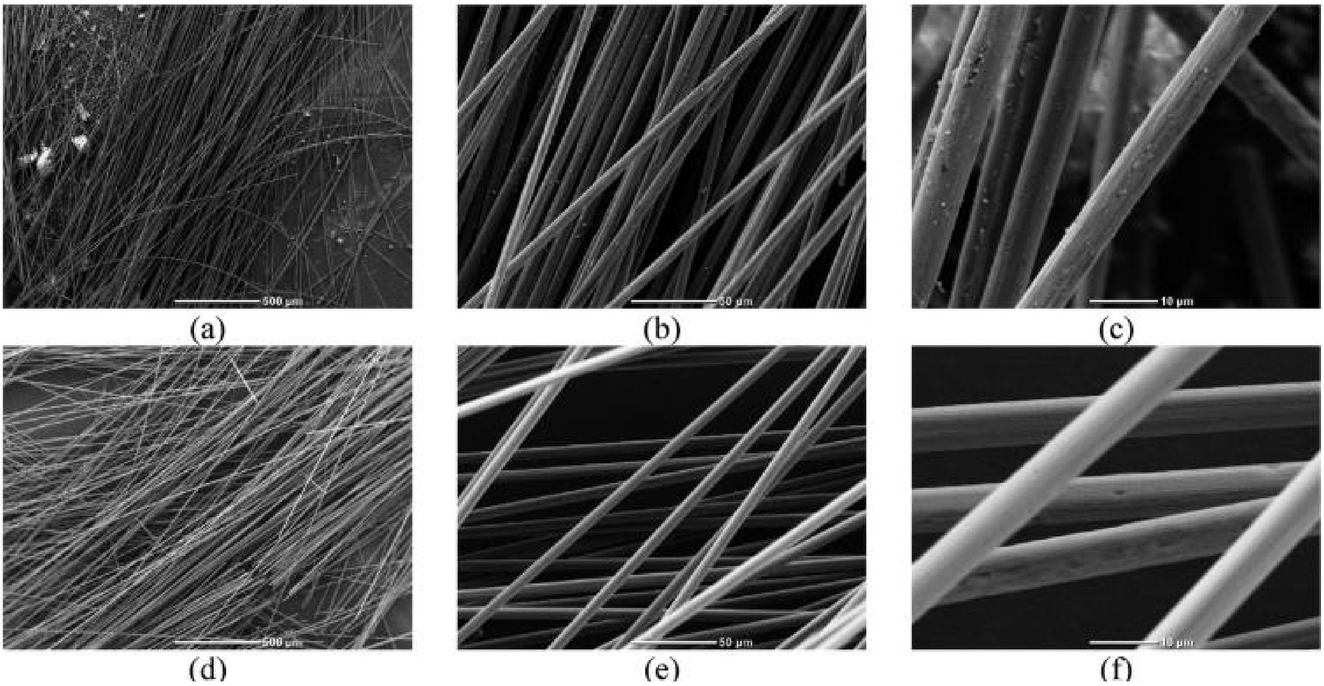


Figure 5-11: SEM images of reclaimed CF for (a, b, and c) pyrolysis up to 800 °C with 20 °C/min heating rate and 30 min isothermal dwelling, and (d, e, f) high effective pyrolysis up to 425 °C followed by oxidation up to 550 °C with 10 °C/min heating rate and 60 min isothermal dwelling [2]

Thanks to all the cited research and to the well-known process, “Guo et al.” [60] analysed not only the effect of different oxidation conditions on the r-CFs properties, but also the characterisation of the pyrolysis products. The schematic of the process is shown in Figure 5-12, in which at a first pyrolysis step (in an Ar atmosphere) follows an oxidation process (in air atmosphere).

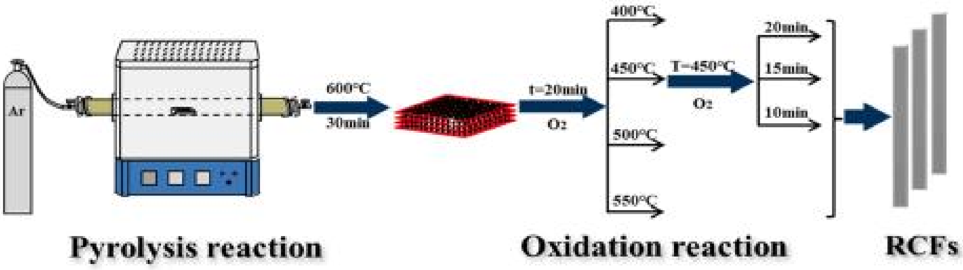


Figure 5-12: Process diagram of carbon fiber recovery by CFRP pyrolysis [60]

Therefore, in Figure 5-13 different surface morphologies can be appreciated, each obtained with different operating conditions and compared to the v-CFs (Figure 5-13a).

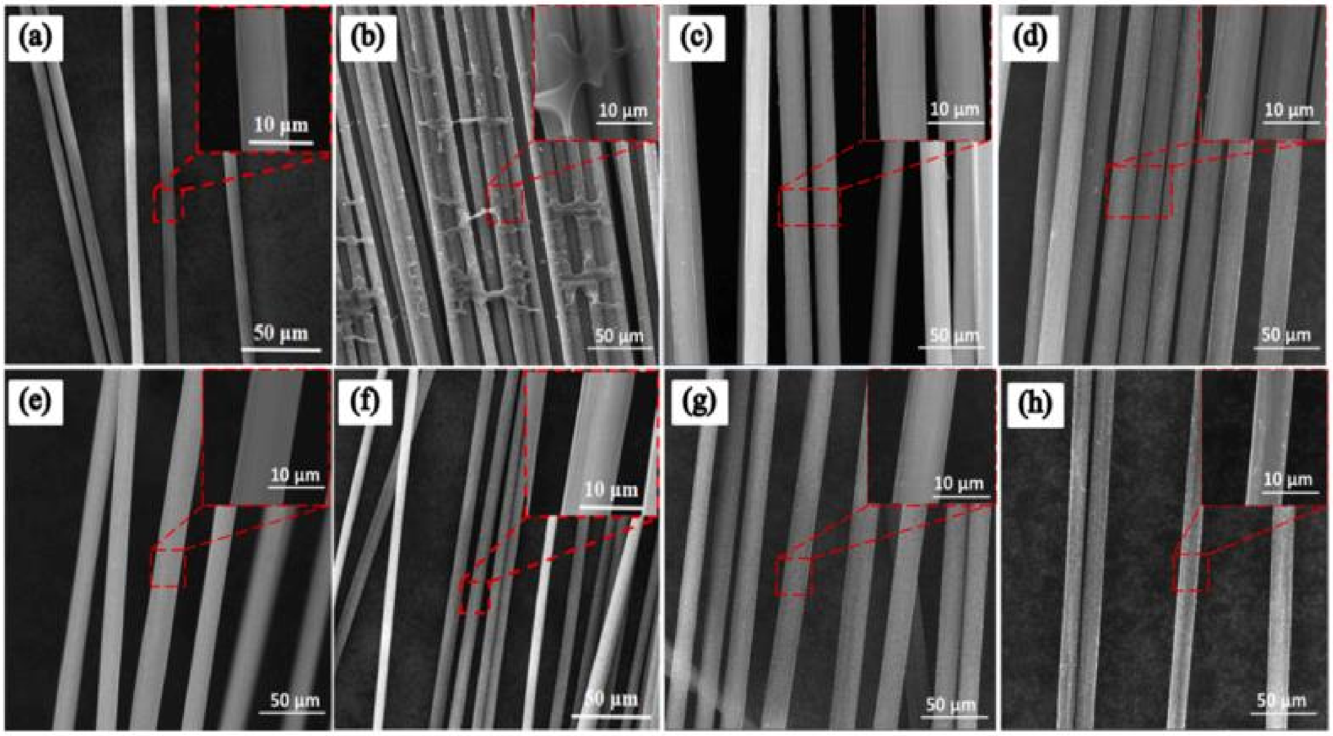


Figure 5-13: The surface morphology of VCF and RCF. (a)VCF; (b)T600t30Ar; (c) T600t30ArT400t20Air; (d) T600t30ArT450t10Air; (e) T600t30ArT450t15Air; (f) T600t30ArT450t20Air; (g) T600t30ArT500t20Air; (h) T600t30ArT550t20Air [60]

The outcome of the experiment highlights that relatively clean r-CFs can be obtained from an oxidation at 450 °C for 15-20 min, with a tensile strength retention higher than 90%, tensile modulus retention above 80% and an electrical conductivity higher or equal to 70% (Figure 5-14).

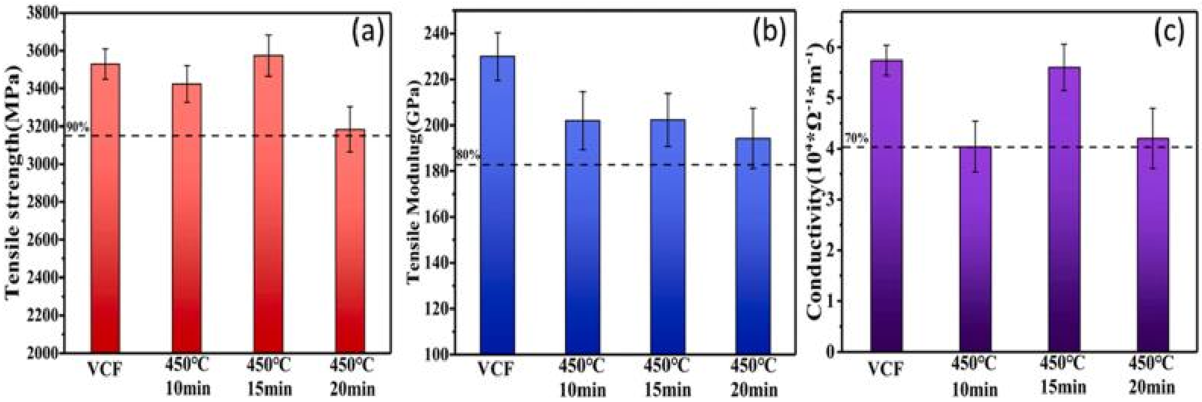
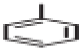
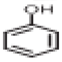
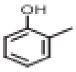
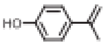
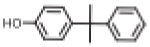
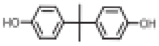
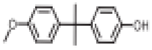
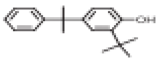
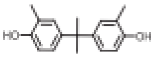
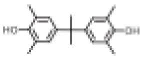


Figure 5-14: Properties graph of VCF and RCF recovered at 450 ◦C. (a) tensile strength; (b) tensile modulus; (c) conductivity [60]

In the end, pyrolysis products were listed in Table 5-3. The epoxy resin matrix is degraded in gas, liquid and carbon products; oxygen-containing aromatic compounds represent the liquid part, while the gaseous part is composed of CO_2. Inside the furnace, organic phases and gases are produced and then discharged as steam. The composition in Table 5-3 is also comparable with the ones that can be found in literature.

Table 5-3: Characterization results of thermal pyrolysis products [60]

Number	Structural formula	Name	Percentage of peak area/%
1	CO_2	Carbon dioxide	3.060
2		Acrolein	1.917
3		1,3-Piperlene	4.094
4		Hydroxypropanone	0.285
5		Methylbenzene	0.606
6		Maleic anhydride	0.201
7		Phenol	1.549
8		2-Methylphenol	0.367
9		4-Isopropylphenol	1.033
10		4-(Prop-1-en-2-yl)phenol	1.874
11		3-Methyltetrahydrophthalic Anhydride	12.696
12		1,2,3,6-Tetrahydro-4-Methylphthalic Anhydride	12.300
13		4-Methylphthalic Anhydride	0.553
14		4-Cumylphenol	0.288
15		Bisphenol A	12.555
16		2-(4'-Hydroxyphenyl)– 2-(4'-methoxyphenyl)propane	4.954
17		2-(1,1-Dimethylethyl)– 4-(1-methyl-1-phenylethyl)- Phenol	0.498
18		4,4'-(1-methylethylidene)	2.821
19		2,2-Bis(4-hydroxy-3,5-dimethylphenyl)propane	3.094

Further modifications of the process can be applied, trying to improve the efficiency of the pyrolysis recycling method. There are some research based on:

- the adjustment of oxygen concentration during pyrolysis process [52].
- The exposition of the CFRPs to superheated steam [52].
- The microwave-assisted pyrolysis (efficient, fast and eco-friendly but still under research) [52],[53].

It seems clear that the pyrolysis technique represents a good choice for the recycling of the CFRP composites for many reasons. It permits to produce long r-CFs with mechanical properties close to the ones of v-CFs, without several damage on the surface. Nevertheless, with this process several amount of CFRPs can be disposed, with higher capacity and recovery rates. Another important aspect relies on the absence of chemical solvents and on the fact that all the products can be reused in whatever form. Besides, the gaseous fraction of the pyrolysis products, can be recovered to satisfy the energy required from the process (fully treated in Chapter 7).

5.3 Fluidised bed process

As mentioned in the previous paragraph, another type of thermal recycling process is the fluidised bed, which is the most well-known implementation. This technique was developed in the mid-1990s at the University of Nottingham [57], in which thorough research led to a deep understanding of different aspects of this process. However, beyond the previously mentioned paper, a collection of more complete data was extracted from [61] but it will be properly used in the next chapter, since energy balances and environmental impact are treated more attentively. Just to give a little spoiler, if the energy required for the recycling of the CFs is generally less than 10%, an optimised fluidised bed process can lead to a reduction of this figure to 3%. [61]. As it is reported in literature, this is the most mature and robust technique based on a continuous process, able to recover high-grade fibers and to deal with polymers containing mixtures of different materials or contaminants. Firstly, as it is mentioned in [52], [53], [61], waste or scrap materials should be reduced to a size in the range of 6 ÷ 20 mm, even if [61] shows how a reduction in the range 1 ÷ 10 mm can be preferred for an optimization of the fluidised bed performance, which is a topic under researc. Then, the scraps enter in the reactor, in which a bed of silica sand (with the size ≃ 850 μm) is fluidised with a hot stream of air (velocity value in the range 0,4 ÷ 1,0 m/s). The stream is heated up at 450 ÷ 550 °C, taking into account the polymers' characteristics, without degrading the CFs properties. Hence, the heat is transferred from the hot stream to the silica particles, so that the epoxy resin is correctly vaporised, and fibers/fillers are released, with a fluffy composition of different lengths and orientation (e.g., a closed loop for r-CFs in the aviation industry can be appreciated in Figure 5-15).

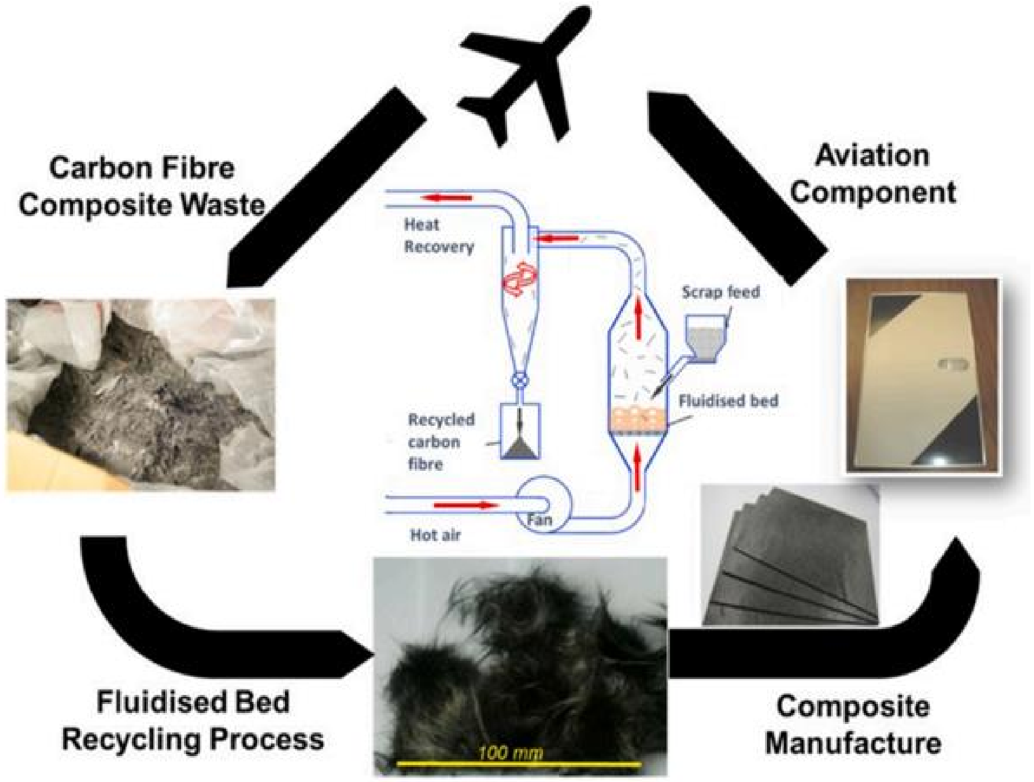


Figure 5-15: The schematic illustration of a fluidised bed thermal process and the closed loop of using r-CF in aviation industry [52]

The fibers are elutriated from the inorganic components (such as aluminium honeycomb, rivets, metal etc.), which are collected at the bottom of the bed and removed by regrading it. Furthermore, the polymeric matrix is vaporised, and the decomposition products are used to recover energy content. Therefore, the gas-solid separation is performed by a cyclone (or other gas-solid devices), which is able to collect fibers and fillers. After that, they are sent to an oxidiser (combustion chamber), so that the polymer decomposition products are fully oxidised at temperature of 750 ÷ 1000 °C. In this way, before being sent to the stack, a certain amount of heat can be recovered from the exhausts to pre-heat the fresh air at the inlet. A clarifying scheme can be found in Figure 5-16.

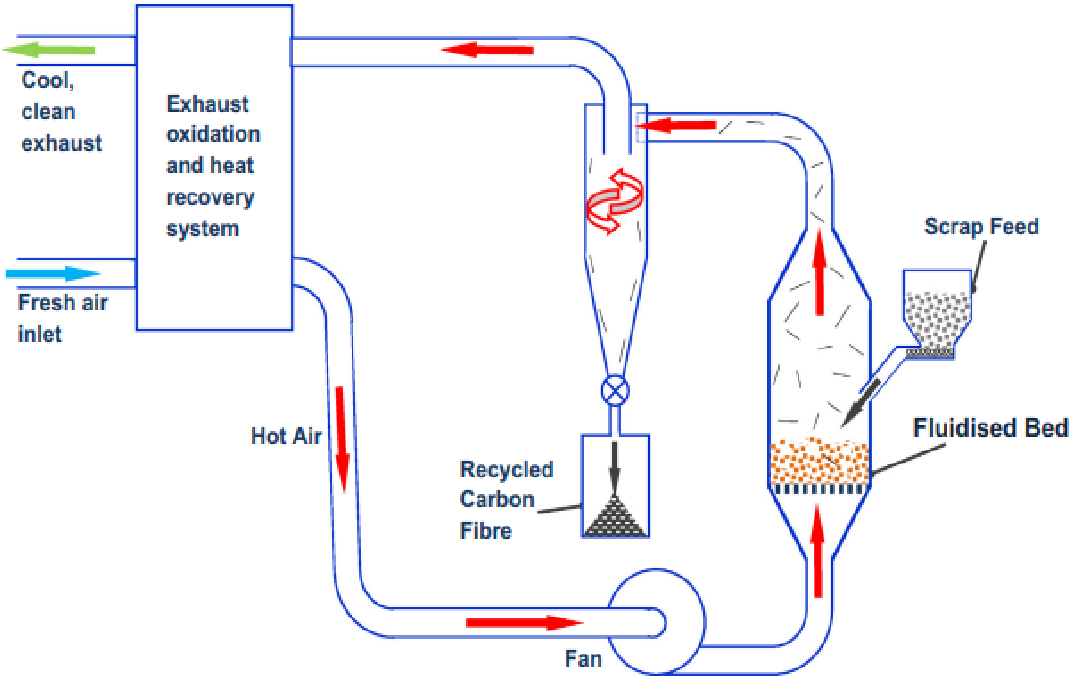


Figure 5-16: Main components and flow directions of the fluidised bed CFRP recycling process [61]

Once the recovered fibers have been subjected to mechanical load testing, SEM and XPS (X-ray Photoelectron Spectroscopy) analyses, different results can be appreciated. Yip et. al [53], [57] found that clean fibers with a mean length in the range 5.9 ÷ 9.5 mm can be obtained. However, a reduction up to 20% in tensile strength were experienced, but with unchanged stiffness (elastic modulus) and surface oxygen content. Furthermore, as Jiang et al. [52] stated that "through this recycling process some of the surface hydroxyl groups on CFs can be transformed to carbonyl (C = O) and carboxylic groups (–COOH) due to the applied heat. However, the interfacial shear strength with epoxy resin did not change" [52]. However, an entire work on the fluidised bed process can be found in [61], which investigates proper mass and energy models in order to evaluate the optimisation of the process. Therefore, this type of technique shows that there are some pros like the one of being able to tolerate mixed and contaminated materials such as end of life vehicle components (Figure 5-15) or to produce fuel gases from the exhausts (recovering energy). However, as long as the CFs from fluidised bed are recovered in "Fluffy form" (at the bottom of Figure 5-15), with an unstructured architecture, as well as some damage in strength and length, the process needs further improvements in order to be cost-effective and to produce high-value r-CFs for CFRPs manufacturing.

5.4 Chemical recycling – Solvolysis process

Last but not least, the remaining recycling techniques that have to be introduced are the chemical ones, based on the solvolysis process (of which common definition can be found in [62], [63]). However, these chemical reactions can be subdivided in solvolysis with supercritical fluids and low temperature solvolysis. To give a brief overview, these two techniques have recently been used in technological areas and are considered to be a way "greener" than the mechanical and thermal ones, due to the absence of pollutant agents in the products. Nevertheless, they are not mature processes (if compared to the others) and nowadays are not indicated for the disposal of large quantities of CFRPs. These features will be dealt with more attentively in the next chapter. As for the solvolysis technique, a huge plethora of research and investigations can be found in literature and the papers used for this report are [52], [53], [57].

Starting in the 90's, a recycling technique for the disposal of FRPs were introduced in Japan [57], based on the use of supercritical fluids. Nowadays, this process has gained more success due to the promising results, providing optimum conditions with fast chemical responses. Before going to the core of this argument, some concepts need to be recapped. Let's start from the definition of supercritical fluid (SFC): "any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist, but below the pressure required to compress it into a solid. It can effuse through porous solids like a gas, overcoming the mass transfer limitations that slow liquid transport through such materials. SCF are much superior to gases in their ability to dissolve materials like liquids or solids. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density" [64] (Figure 5-17).

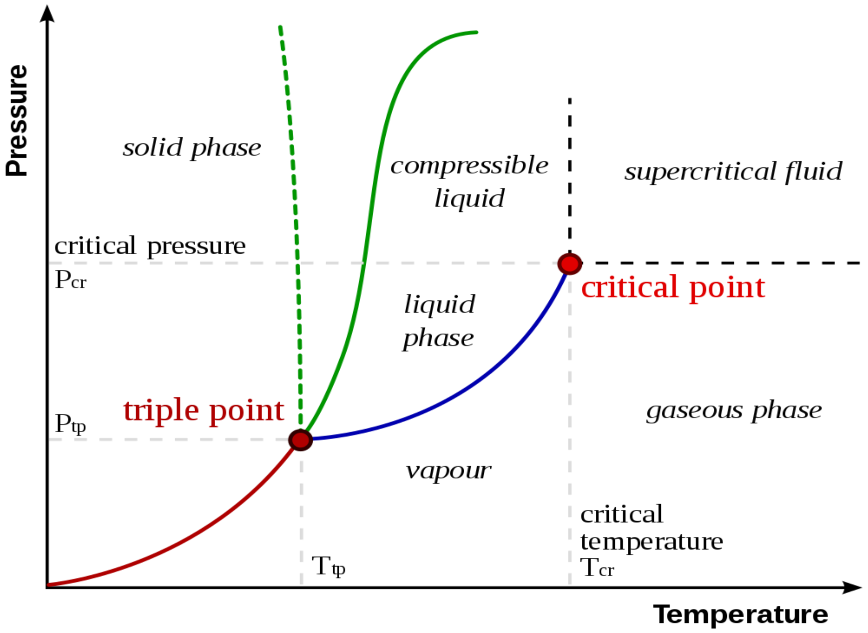


Figure 5-17: The liquid–vapor critical point in a pressure–temperature phase diagram is at the high-temperature extreme of the liquid–gas phase boundary. The dashed green line shows the anomalous behaviour of water [65]

The properties of some common solvents at their critical point can be found in Table 5-4 (extracted and readapted from [62]).

Table 5-4: Critical properties of various solvents, extracted from [16]

SOLVENT	**MM [g/mol]**	**T_C [K]**	**p_C [MPa]**	**ρ_C [g/cm^3]**
Carbon dioxide	44.01	304.1	7.38	0.469
Water (H_2O)	18.015	647.096	22.0.64	0.322
Methane (CH_4)	16.04	190.4	4.60	0.162
Ethane (C_2H_6)	30.07	305.3	4.87	0.203
Propane (C_2H_6)	44.09	369.8	4.25	0.217
Ethylene (C_3H_8)	28.05	282.4	5.04	0.215
Propylene (C_3H_6)	42.08	364.9	4.60	0.232
Methanol (CH_3OH)	32.04	512.6	8.09	0.272
Acetone (C_3H_6O)	58.08	508.1	4.70	0.278
Ammonia (NH_3)	17.03	405.56	11.36	0.244

Hence, thanks to the peculiar features of the supercritical fluid (liquid-like density, gas-like viscosity, high diffusivity), solvolysis induces to the rapid and selective breaking down of the polymeric matrix. Polymers obtained from condensation polymerization, such as PET, nylon and polyurethane can be depolymerized into high yield monomers. The ones obtained from addition polymerization, such as phenol and epoxy resins, polyethylene can also be degraded into the initial monomers. CFRPs can be decomposed into smaller molecular pieces or fibers. Therefore, when using near- and supercritical-fluids (like water, alcohols, ammonia, organic solvents) at different operative conditions, the final products will be dissolved in depolymerised resins and monomers, inorganic fillers and fibers with a removal efficiency between 95% and 100% (as reported in literature). It is true that this is a promising process, able to produce high quality r-CFs, but the industrial readiness is less than the one of the other recycling processes, since requires particular types of reactors (i.e., semi continuous flow reactors, depicted in Figure 5-18), able to operate at high temperatures and with corrosive media.

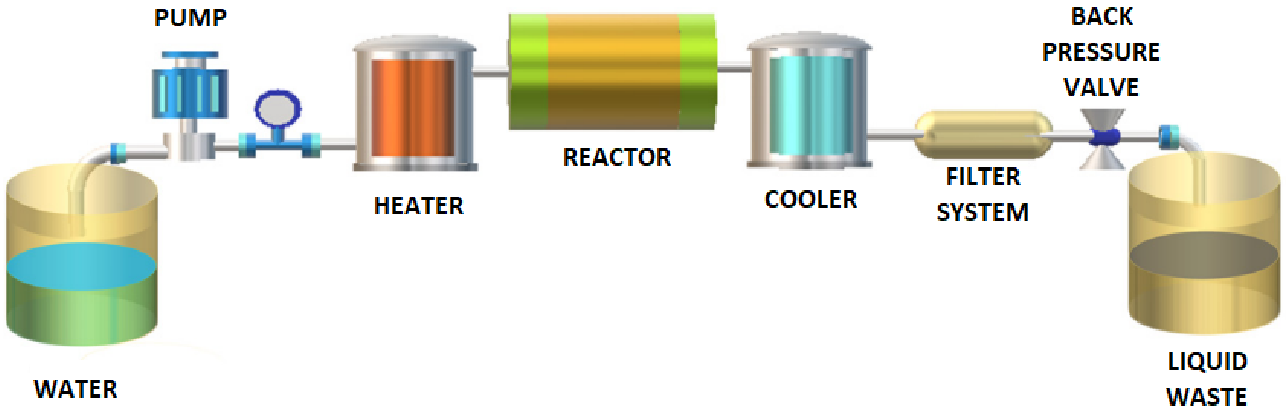


Figure 5-18: Example of semi-continuous flow reactor, extracted and readapted from [57]

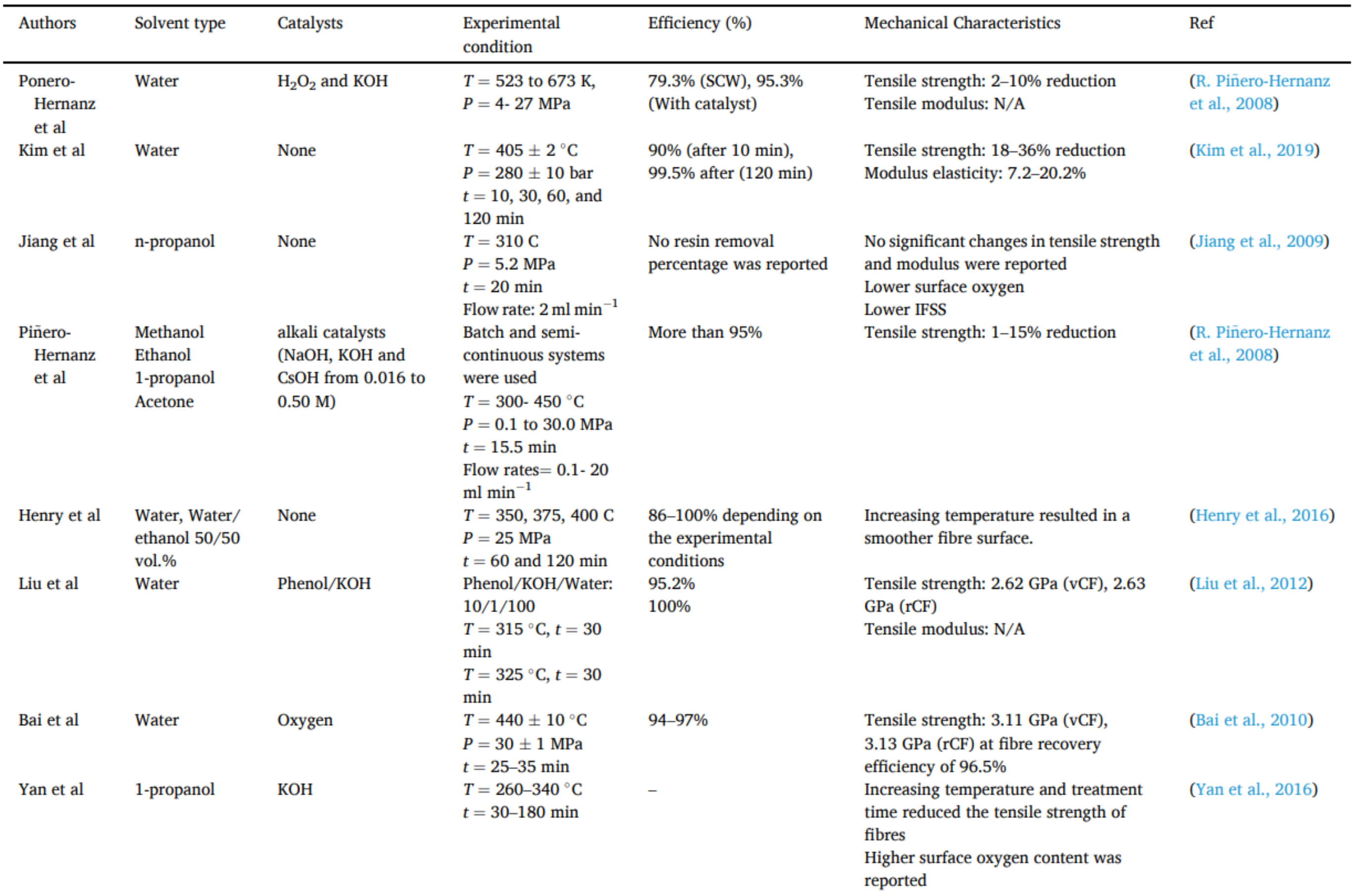
To sum up, the main advantages of using SCFs are:

- Obtaining clean fibers with good retention of mechanical properties.
- Maintaining the length of the fibers fed to the reactors.
- Achieving of a rapid and selective chemical reaction (depolymerisation).

5.4.1 Solvolysis with supercritical water and alcohols

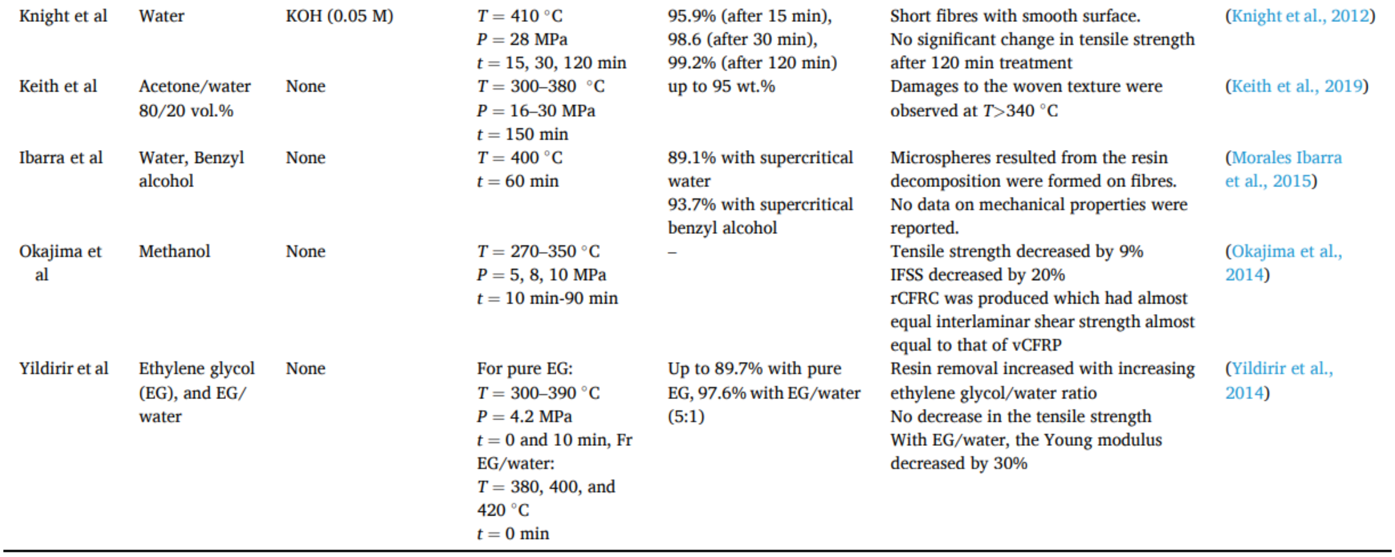
As it is reported in the referenced literature, different experiments/investigations have been performed in order to find the optimum operative conditions at which CFs can be recovered. Different solvents can be used but, among all of them, the efficiency of water and alcohols have been studied with more attention. The mentioned papers report processes using supercritical water or alcohols. Water is preferred for its non-toxicity and recyclability and also because for its dielectric constant, that reduces above the critical point and let it acts as a non-polar solvent. Otherwise, alcohols can be preferred since are easier to treat because of their lower critical point conditions (i.e., 200 - 300 °C and 2.0 - 6.0 MPa [52]) compared to water. Obviously, using those fluids, the environmental impact should be taken into account. Some research will be mentioned, so that the key parameters for the optimization of this process can be fully understood. Some publications concerning the reclamation of CFs using solvolysis method are provided in Table 5-5 and Table 5-6.

Table 5-5: Some publications on reclaiming CF from CFRC using solvolysis method [52]



Authors	Solvent type	Catalysts	Experimental condition	Efficiency (%)	Mechanical Characteristics	Ref
Ponero-Hernanz et al	Water	H_2O_2 and KOH	$T = 523$ to 673 K, $P = 4$- 27 MPa	79.3% (SCW), 95.3% (With catalyst)	Tensile strength: 2–10% reduction Tensile modulus: N/A	(R. Piñero-Hernanz et al., 2008)
Kim et al	Water	None	$T = 405 \pm 2\,^{\circ}C$ $P = 280 \pm 10$ bar $t = 10$, 30, 60, and 120 min	90% (after 10 min), 99.5% after (120 min)	Tensile strength: 18–36% reduction Modulus elasticity: 7.2–20.2%	(Kim et al., 2019)
Jiang et al	n-propanol	None	$T = 310$ C $P = 5.2$ MPa $t = 20$ min Flow rate: 2 ml min^{-1}	No resin removal percentage was reported	No significant changes in tensile strength and modulus were reported Lower surface oxygen Lower IFSS	(Jiang et al., 2009)
Piñero-Hernanz et al	Methanol Ethanol 1-propanol Acetone	alkali catalysts (NaOH, KOH and CsOH from 0.016 to 0.50 M)	Batch and semi-continuous systems were used $T = 300$- 450 °C $P = 0.1$ to 30.0 MPa $t = 15.5$ min Flow rates= 0.1- 20 ml min^{-1}	More than 95%	Tensile strength: 1–15% reduction	(R. Piñero-Hernanz et al., 2008)
Henry et al	Water, Water/ ethanol 50/50 vol.%	None	$T = 350$, 375, 400 C $P = 25$ MPa $t = 60$ and 120 min	86–100% depending on the experimental conditions	Increasing temperature resulted in a smoother fibre surface.	(Henry et al., 2016)
Liu et al	Water	Phenol/KOH	Phenol/KOH/Water: 10/1/100 $T = 315\,^{\circ}C$, $t = 30$ min $T = 325\,^{\circ}C$, $t = 30$ min	95.2% 100%	Tensile strength: 2.62 GPa (vCF), 2.63 GPa (rCF) Tensile modulus: N/A	(Liu et al., 2012)
Bai et al	Water	Oxygen	$T = 440 \pm 10\,^{\circ}C$ $P = 30 \pm 1$ MPa $t = 25$–35 min	94–97%	Tensile strength: 3.11 GPa (vCF), 3.13 GPa (rCF) at fibre recovery efficiency of 96.5%	(Bai et al., 2010)
Yan et al	1-propanol	KOH	$T = 260$–340 °C $t = 30$–180 min	–	Increasing temperature and treatment time reduced the tensile strength of fibres Higher surface oxygen content was reported	(Yan et al., 2016)

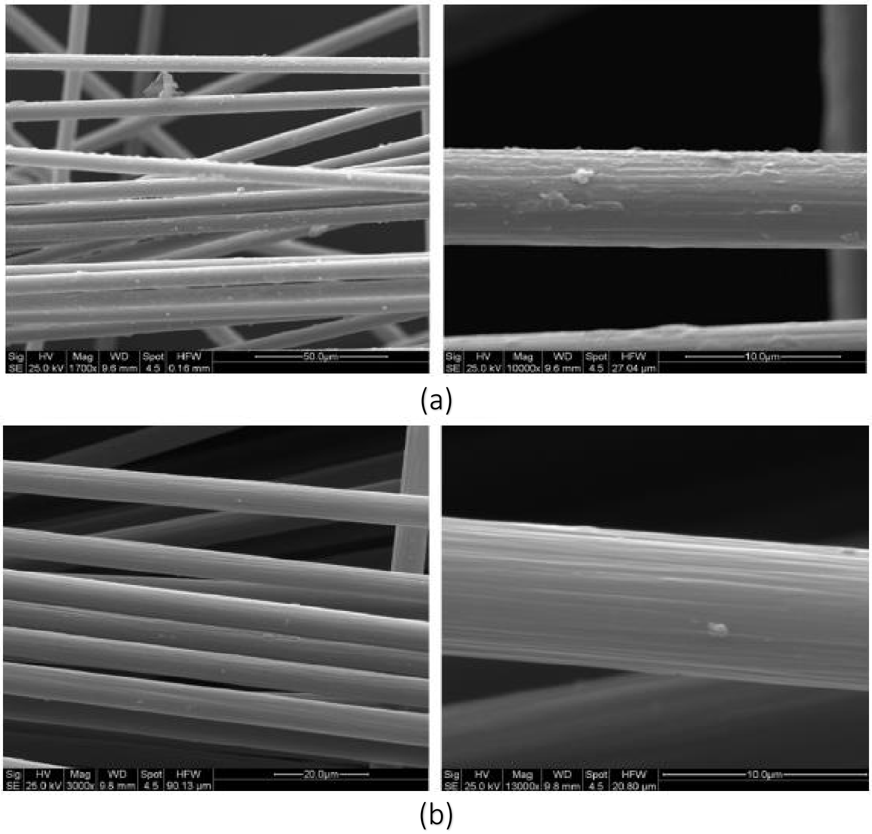
Table 5-6: Some publications on reclaiming CF from CFRC using solvolysis method [52]



Knight et al	Water	KOH (0.05 M)	$T = 410\ ^\circ C$ $P = 28$ MPa $t = 15, 30, 120$ min	95.9% (after 15 min), 98.6 (after 30 min), 99.2% (after 120 min)	Short fibres with smooth surface. No significant change in tensile strength after 120 min treatment	(Knight et al., 2012)
Keith et al	Acetone/water 80/20 vol.%	None	$T = 300–380\ ^\circ C$ $P = 16–30$ MPa $t = 150$ min	up to 95 wt.%	Damages to the woven texture were observed at $T > 340\ ^\circ C$	(Keith et al., 2019)
Ibarra et al	Water, Benzyl alcohol	None	$T = 400\ ^\circ C$ $t = 60$ min	89.1% with supercritical water 93.7% with supercritical benzyl alcohol	Microspheres resulted from the resin decomposition were formed on fibres. No data on mechanical properties were reported.	(Morales Ibarra et al., 2015)
Okajima et al	Methanol	None	$T = 270–350\ ^\circ C$ $P = 5, 8, 10$ MPa $t = 10$ min-90 min	–	Tensile strength decreased by 9% IFSS decreased by 20% rCFRC was produced which had almost equal interlaminar shear strength almost equal to that of vCFRP	(Okajima et al., 2014)
Yildirir et al	Ethylene glycol (EG), and EG/water	None	For pure EG: $T = 300–390\ ^\circ C$ $P = 4.2$ MPa $t = 0$ and 10 min, Fr EG/water: $T = 380$, 400, and 420 °C $t = 0$ min	Up to 89.7% with pure EG, 97.6% with EG/water (5:1)	Resin removal increased with increasing ethylene glycol/water ratio No decrease in the tensile strength With EG/water, the Young modulus decreased by 30%	(Yildirir et al., 2014)

In 2002, the studies on the reclamation of CFs from CFRPs using sub-supercritical water was started by Okajima et al. [53], [57]. The fibers were recovered at the temperature of 380 °C and 25 MPa. Pinero-Hernanz et al. (2008) [66] studied supercritical water in the temperature range 250 – 400 °C with a pressure of 4 – 28 MPa, in presence of hydrogen peroxide (H_2O_2). The authors performed the experiment with and without catalyst (potassium hydroxide - KOH), of which concentration has been found to be the most important variable in the process. The results showed that the presence of H_2O_2 negatively affected the overall yield, while temperature and time were the most influential parameters. It has been found that the catalyst significantly improved the removal efficiency but worsen the retention in tensile strength. So, without KOH the remove yield was of 79.3% with a loss in tensile strength of 2%. While using the catalyst, the efficiency increased to 95.4% but the tensile strength decreased of 10% compared to the v-CFs. In Figure 5-19a and Figure 5-19b, the effect of the alkali catalyst can be appreciated. Further and precise information can be found in [66].

Some other authors (that can be found in [52], [53], [57]) have researched the impact of other catalyst such as sulphuric acid, KOH/phenol and oxygen on improving the solvolysis process. Therefore, acting on the catalyst concentration will directly affect the efficiency maximisation. Liu et al. [67] have found that using phenol for 30 min treatment at 315 °C, can lead to an efficiency of 95.2%. While using KOH as catalyst, for the same time but at a temperature of 325°C, the 100% of removal efficiency can be reached, with mechanical properties and surface morphology comparable with those of v-CFs. More information about this investigation in [67].



(a)

(b)

Figure 5-19: (a) SEM micrograph of the reclaimed carbon fibres after supercritical-water treatment in batch a reactor at 673 K, 27 MPa (solvent volume 3 mL, reaction time 30 min); (left) reclaimed fibres at 1700x magnification: some small deposits of residual epoxy resin remain on the surface (79.3 wt.% eliminated resin). (right) Close-up view of a single carbon fibre (at 10,000x magnification): the fibre is 7–8 µm in diameter; the surface seems not to be damaged but is quite impregnated with residual polymer [66].

(b) Recycling of carbon fibres in supercritical water with an alkali catalyst (KOH 0.5 M) at 673 K, 27.5 MPa and reaction time 15.5 min. (left) SEM micrograph (at 3000x magnification); as seen, the fibres surface is well-preserved and almost resin free (95.4 wt.% of eliminated resin). (right) image at 13,000x magnification close-up view of a single carbon fibre; the diameter of the fibre is kept constant (7–8 µm) and the surface did not exhibit any damage or fissure [66]

Furthermore, experiments like the one conducted by Morin et al. [53] demonstrate that it is possible to obtain high quality r-CFs, with a clean surface and mechanical properties, which are close to the one of the v-CFs. As shown in Figure 5-21, by means of a semi-continuous flow reactor (Figure 20), excellent results can be achieved.

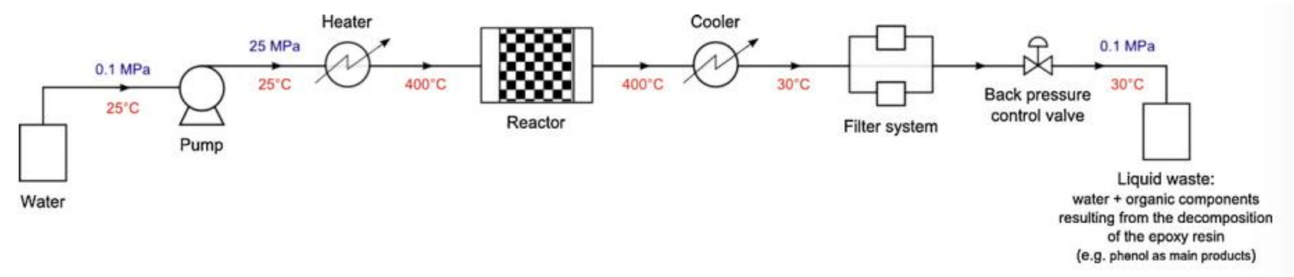


Figure 5-20: A schematic flow diagram for the recycling process [53]

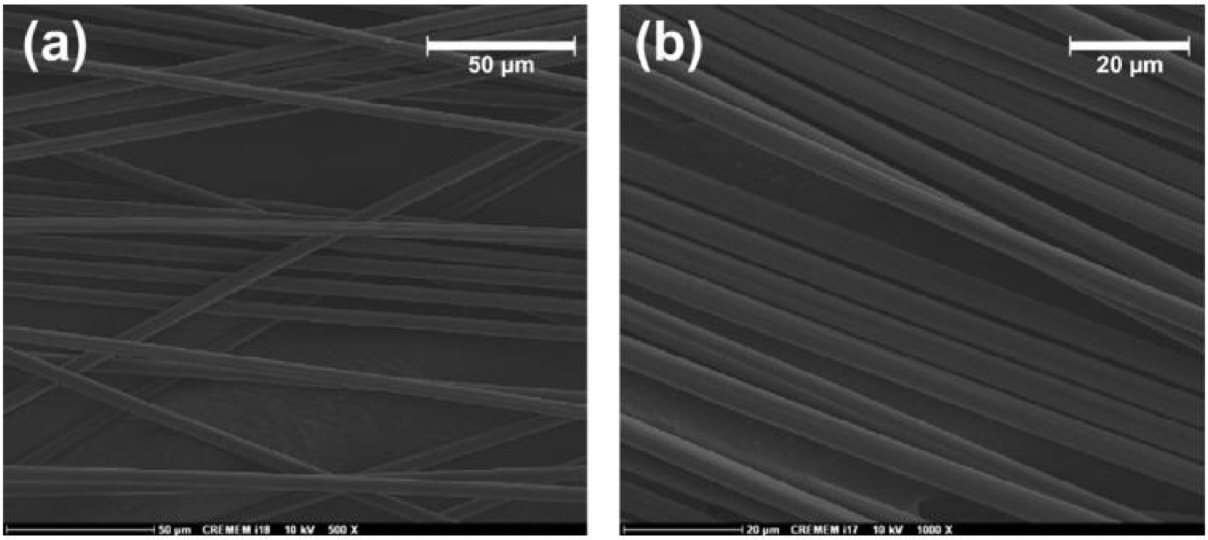


Figure 5-21: SEM micrograph (500×) of the recycled carbon fibres treated with sc-water at 400°C, 25 MPa and at a reaction time of 30 min (a) a close up (1000×) of the recovered fibres (b) shows that the recycled fibres are clean. [7]

Similarly, a huge plethora of research can be found for the solvolysis in presence of alcohols. A group of papers can be found in [52], [53], [57], whose authors have tried to obtain r-CFs with good retention of mechanical properties and clean surface, with or without the usage of alkali catalyst. Obviously, as it was mentioned above, the critical coordinates of alcohols are lower than those of water. Hence, applying an alcoholysis process can lead to a less expensive process. Nowadays it can be more promising to reproduce a hydrolysis process, which is greener and safer. However, all those mentioned research have been carried out at lab scale. Further studies need to be undertaken to reach the industrial readiness for this process and to make it cost-effective.

5.4.2 Low temperature solvolysis

The application of supercritical fluids as reaction media results to be, not only more eco-friendly, but also more manageable and efficient. Nevertheless, it is also true that this type of process needs specific facilities, since both pressure and temperature should be optimized, leading to an energy-intensive process. Due to this, some other research was based on the low temperature solvolysis, which is still way more efficient compared to thermal and mechanical processes, but the solvents used for the chemical degradation can be toxic and aggressive. However, using different types of solvents along with catalysts, easier experimental conditions can be achieved. Just to facilitate the interaction of catalysts and oxidants, the swelling of the CFRPs is induced by means of pre-treatments. Therefore, the bonds are broken by means of the catalysts, which diffuse inside the cross-linked network. Due to that, acids and alkali are used to enhance the decomposition of the network.

Focusing on [52], various investigation carried by different authors can be found. E.g., Jiang et al. in 2017 have tried the decomposition of CFs/epoxy resin composites by means of acid/sulphuric acid mixture, treating the products with polyethylene glycol (macrogol 400) and KOH (Figure 5-22). Carrying the process at a temperature of 160°C for 200 min, CFs were obtained with a removal efficiency of 97% and a reduction in tensile strength of 4%.

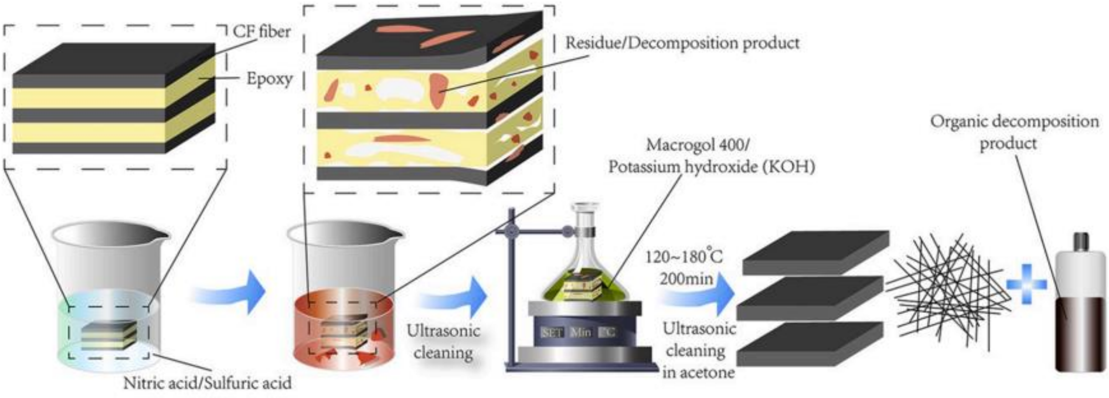


Figure 5-22: Recovery of CFs using nitric acid and macrogol 400 [52]

Li et al. have found that H_2O_2 is able to enhance the polymer degradation, better in presence of additional heat or catalyst. Furthermore, Xu et al. investigates the reaction of H_2O_2, which generates hydroxyl radicals, a group able to oxides organic compounds. Also, Zabihi et al. have found that the decomposition process using H_2O_2/Tartaric Acid, can be accelerated by means microwave irradiation (Figure 5-23), leading to promising results. In the same paper, another implementation is introduced by Das and Varughese, which have examined the ultrasonication in liquids in presence of nitric acid (e.g., a recovery process in presence of nitric acid can be found in [54]) (Figure 5-24).

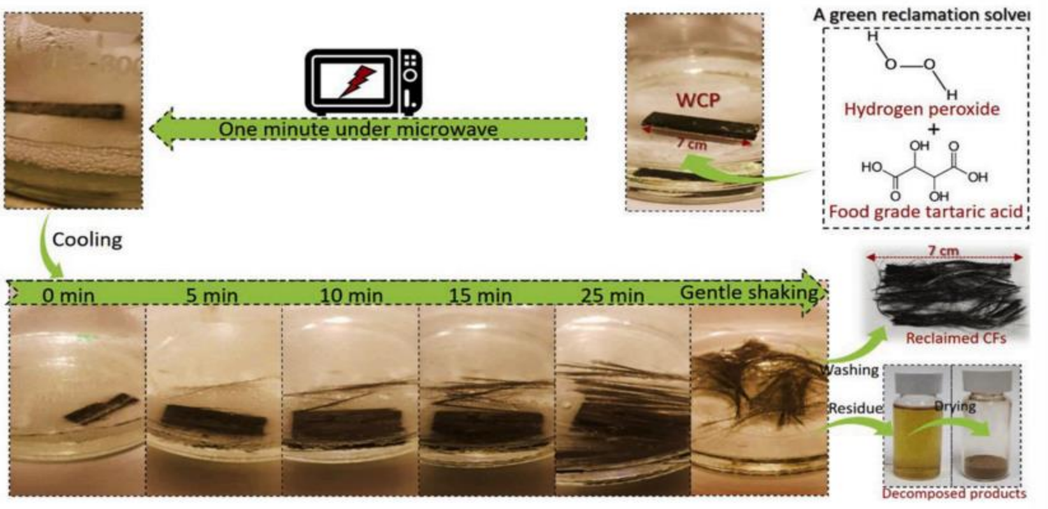


Figure 5-23: Microwave assisted recovery of CF from waste composite parts in the presence of H2O2/TA as solvent [52]

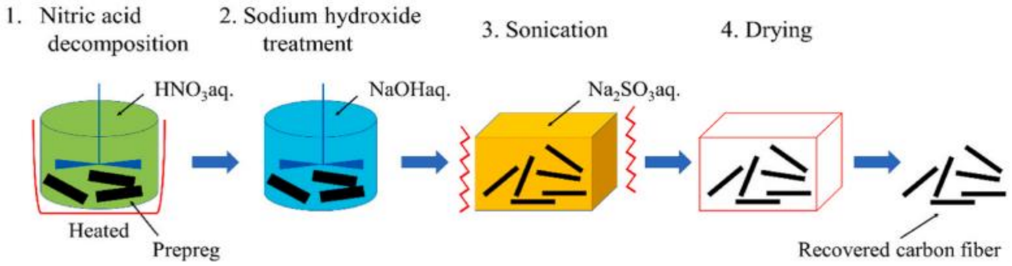


Figure 5-24: Schematic of carbon fiber recovering process using nitric acid in a reactor vessel [54]

However, the choice of the catalyst and solvent types is crucial in determining the removal efficiency. As can be seen in literature, mainly in [52], Wang et al. and Liu et al. carried investigations on different types of solvents and catalyst (such as KOH, nitric acid, $ZnCl_2$, $AlCl_3$ and $FeCl_2$). Furthermore, in Figure 5-25 the swelling rate in function of different solvents can be appreciated, and it can be seen that acetic acid is able to reach ≃ 50%. If accompanied by $AlCl_3$, acetic acid is able to reach 100% of the removal efficiency. Liu et al. [52] have found that $ZnCl_2$ is more efficient in breaking down the CFRPs and that ethanol can be preferred to water due to the enhancing of the interaction between catalyst and chemical bonds. Another interesting research can be found in [48], in which CFRPs composites coming from aerospace field are recycled. "The composite samples were added into glacial acetic acid, taking the pre-treatment process first, and then the pre-treated CFRP composite samples were wholly degraded in KOH/MEA solvent system" (Figure 5-25 and Figure 5-26). More information about the process can be found in [48].

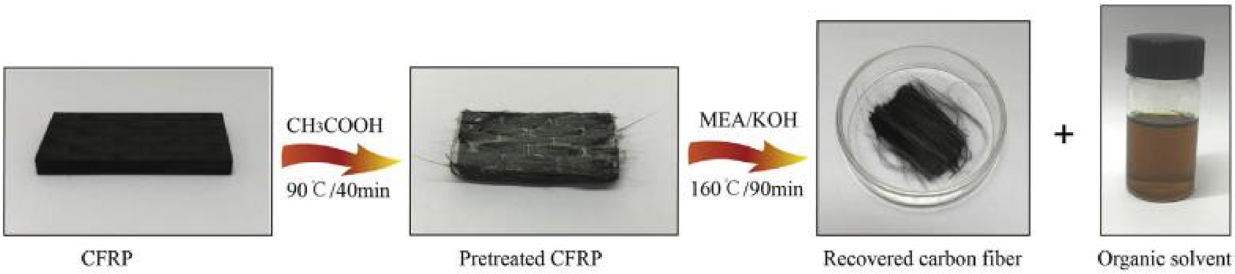


Figure 5-25: Recycling process of the CFRPs taken from [48]

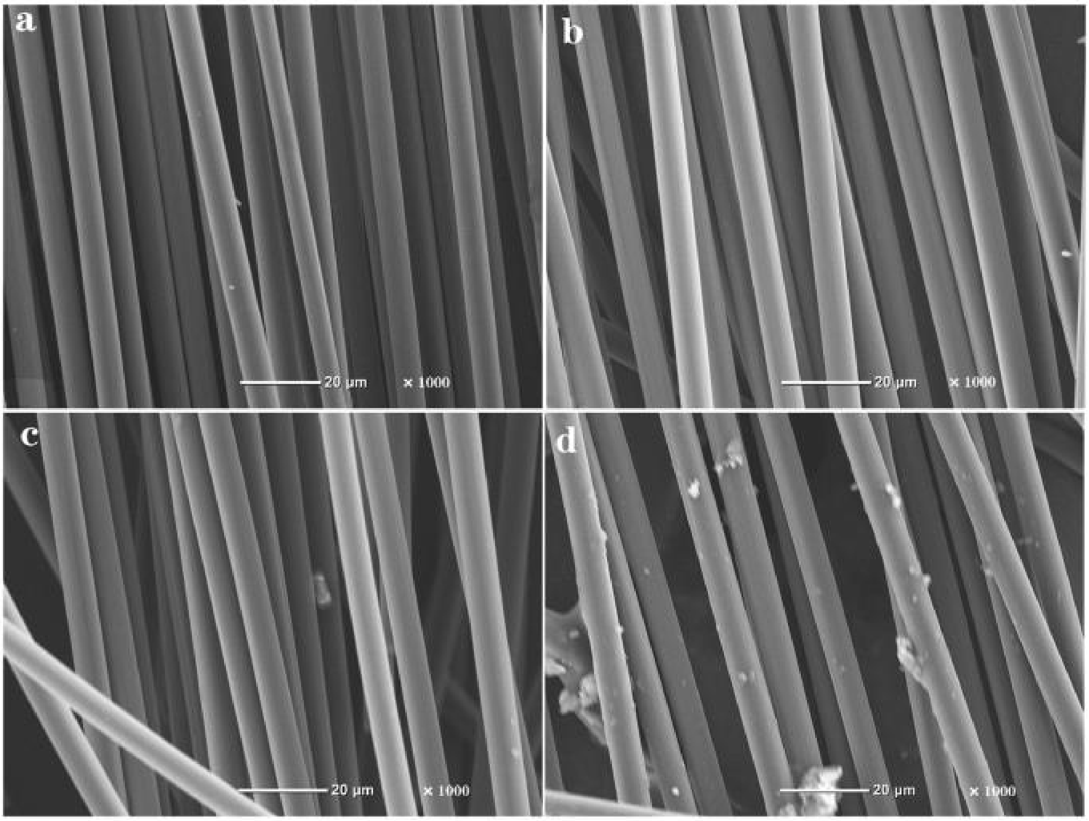


Figure 5-26: SEM image of a virgin CFs; b, c and d recovered CFs obtained after degradation at 170 °C, 160 °C and 150 °C for 90 min respectively [48]

6. Economic and environmental perspectives of recycling techniques

The aim of the afore-mentioned recycling techniques is to obtain recovered CFs with characteristics as closer as possible to the ones of the virgin CFs. By doing so, the diffusion of high-quality r-CFs in different fields (according to governmental applicability) will increase. Therefore, as it was mentioned before, the nowadays literature on these topics is not as rich as it could be expected and suffers of lack of information that can help in the understanding of the feasibility of the single processes. Some authors, like Vo Dong et al. [58], have performed Life Cycle Assessment (LCA) and Life Cycle Cost (LCC) analyses, "employed as standard methods to assess the environmental and financial benefits of CFRCs recycling methods. They are well-established approaches which quantify the environmental and economic aspects of products considering each stage of their manufacturing process" [52]. However, recycling techniques are often compared with incineration and landfilling, which have the lowest operating costs (due to this, along with the lack of clear market outlook, recycling of CFRPs is a costly and unattractive procedure). Advantages and disadvantages of the main recycling techniques were discussed in depth in previous chapters. Among those methods, even if it leads to the lowest processing costs, mechanical recycling is not suitable for high-value application due to the severe damage of the fibers and the unclear matrix-reinforcement separation. Solvolysis with supercritical water (SCW) is the most trending method, since it is cheap and of low-hazardous risk, providing the highest valued r-CFs. The barrier for this process is represented by the energy requirements and mainly by the low processing rate. Hence, the best process is probably represented by pyrolysis, which is the most successfully industrialized method that permits to obtain high-value r-CFs with an excellent retention of mechanical properties. Some limitations are represented by the high energy consumption, even if it permits the possibility to recover energy from the exhausts. Furthermore, microwave pyrolysis is another promising treatment (mentioned in the chapter 5.2 dedicated to pyrolysis), which permits to reduce two thirds of the energy requirements with respect to the conventional pyrolysis. Thanks to the reports provided by Vong et al. [58] and some of the afore-mentioned authors, it is possible to appreciate some figures to speak in terms of energy. The energy consumption for each recycling process is reported in Table 6-1 (extracted from [57], [58] and rearranged), remembering that the embodied energy of v-CFs is in the range 183–286 MJ/kg of carbon fibers. While in Table 6-2 (extracted from [58] and rearranged) the investment costs for each method are listed.

Table 6-1: Energy consumption during recycling of CFRPs [57], [58]

	Energy consumption
Mechanical recycling **(cutting energy by milling machine)**	$0.27 \div 2.03\ MJ/kg$
Fluidised bed	$14.4\ MJ/kg$
Chemical recycling	$60 \div 90\ MJ/kg$
Solvolysis	$19.2\ MJ/kg$
Microwave pyrolysis	$10\ MJ/kg$
Pyrolysis	$3 \div 30\ MJ/kg$

Table 6-2: Investment cost for process in literature [58]

	Investment cost	Capacity
Mechanical (grinding)	200 000 €	4000 $ton/year$
Pyrolysis	10 000 €	20 000 ÷ 80 000 $ton/year$
Microwave	9 400 000 £	50 000 $ton/year$
Supercritical water	5 770 000 $	150 $kg/hour$

As for the economic assessment, the paper of reference in this topic will be the one written by Vong et al. [58]. For sake of simplicity, since it is not the focus of this report, Figure 6-1 is used to give an idea of the current scenario (see the mentioned paper for further information). However, for a better understanding, three economic indicators are introduced:

- Operation Cost (OC) – referred to the mass unit of waste, “is the cost of input utilities required by each recycling technique” [58].
- Average Unit Cost per mass unit of waste (UCW) – “for non-Recovery techniques, this indicator corresponds to the total fees charged by government or the concerned industry; for Recovery pathways, this indicator is the breakeven point charged to an amount of waste through a 10-year horizon time of recycling plant for Recovery pathways” [58], corresponds to the null value of the Net Present Value (NPV) with a discount rate of 10% (Equation 9).

$$\frac{REVENUES\ (at\ NPV=0)}{Waste\ input\ capacity}\quad \text{(for Recovery pathway)} \tag{9}$$

- Average Unit Cost per mass unit of recovered fiber (UCF) - “only concerns Recovery Pathways, which is the average cost of recovered fibre during 10-year horizon time so that recycling plants can cover all their manufacturing cost and begin to have profit” [58] (Equation 10). In this case, UCF is used to underline the acceptable price at which r-CFs can be sold and applied in order to promote recycling and the market of r-CFs.

$$\frac{REVENUES\ (at\ NPV = 0) - \sum(Revenue\ of\ other\ products)}{Recovered\ fiber\ capacity} \tag{10}$$

In Table 6-3 (extracted from [58] and rearranged), the average price of virgin carbon fibers (differed by grades and properties) is compared with the UCF indicator. Further information such as the price gap between the different CFs types can be found in [58].

Table 6-3: Price ranges of CFs in market [58]

Type of fiber	Price
v-CF (low modulus)	$< 20\ \$/kg$
v-CF (standard modulus)	$20 \div 55\ \$/kg$
v-CF (intermediate modulus)	$55 \div 65\ \$/kg$
v-CF (high modulus)	$65 \div 90\ \$/kg$
v-CF (ultra-high modulus)	$up\ to\ 2000\ \$/kg$
Low-cost CF	$4.5 \div 7.5\ \$/kg$
v-CF (from lignin precursor)	$6.6\ \$/kg$
r-CF (from thermo /chemical process)	$\mathbf{13 \div 19\ \$/kg}$

Taking a first look at Figure 6-1, as could be expected, recycling methods are not cost-competitive yet, due to the presence of landfilling and incineration. The owners that do not have any economic interest in recycling or stock the composites, only have to spend roughly 0.1 €/kg, a price that set landfilling and incineration the most competitive choice for the CFRPs treatment. Therefore, until no regulation in the market is imposed, these two methods will continue to be the main choice in CFRP waste management. Landfill and incineration will be neglected only when r-CFs will become profitable.

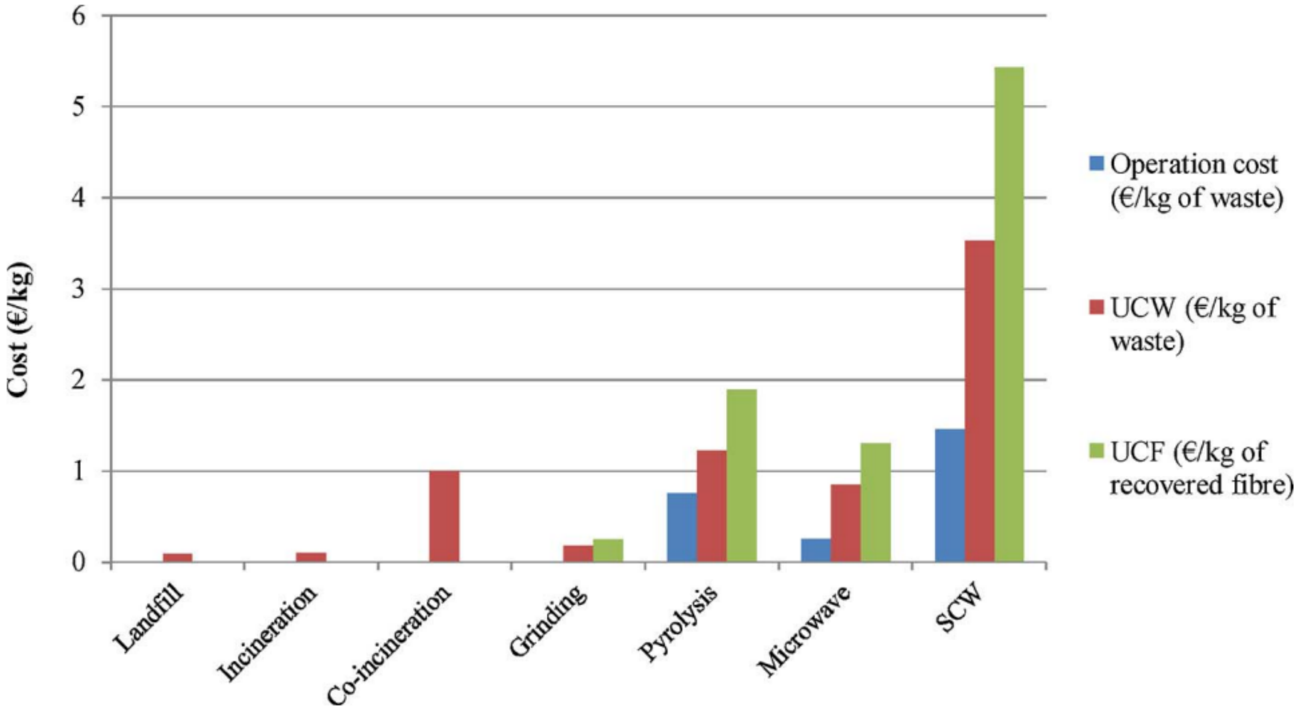


Figure 6-1: Economic assessment of CFRPs recycling techniques [58]

Co-incineration loses economic interest with its 1 €/kg, since it allows waste recovery both from energy and material view (it represent a more interesting way to incinerate the composite). Focusing on the recycling pathways, grinding represents the method with the lowest energy consumption and so with the lowest OC. It also shows the smaller UCW among the recycling methods because of the simple equipment and high capacity, with an UCF at 0.248 €/kg (roughly equal to the price of recovered glass fibers). Due to the disadvantages related to mechanical recycling, the recovered fibers are used in low value applications. Further, conventional pyrolysis and solvolysis with SCW show the higher OC, since consistent operative conditions are needed (high T and p), especially for SCW. The UCF for recovered fibers from thermal processes is lower than the threshold represented by the lower price of 4.5 €/kg (see Table 6-3), used for general applications. Takin into account the assumptions done by the authors in [58], the UCF of the r-CFs from SCW is equal to 5.43 €/kg (the highest among the recovery pathways), which exceed the threshold of the lower price for r-CFs. The highest costs related to solvolysis process are related to the high utility cost, high investments, and small capacity. Although, microwave pyrolysis represents an attracting choice if compared to the conventional methods (with roughly the same capacity). OC and UCW are lower due to the energy reduction in using the microwave heating (1/3 of the pyrolysis).

The two opposites are represented by mechanical recycling and SCW, with the lowest and highest UCF respectively. The r-CFs with the highest quality are obtained through solvolysis with SCW, with properties close to those of the v-CFs. Unfortunately, this technique needs further improvements to become more competitive than methods like pyrolysis. It must be noticed that the UCF values are yet lower than the value of the r-CFs showed in Table 6-3. This gap can be clarified reading the dedicated section in [58]. This indicator strictly depends on the installed capacity and increasing the capacity the UCF will decrease. Then, in [58] the recovery rate (with a value between 10% and 100%) is analysed with a fixed capacity of 2000 t/year for all the recovery methods. The carbon fiber recovery rate represents the r-CFs fraction used for CFs applications. The remaining part is considered to replace glass fibers. The sensitivity study can be better understood looking at Figure 6-2.

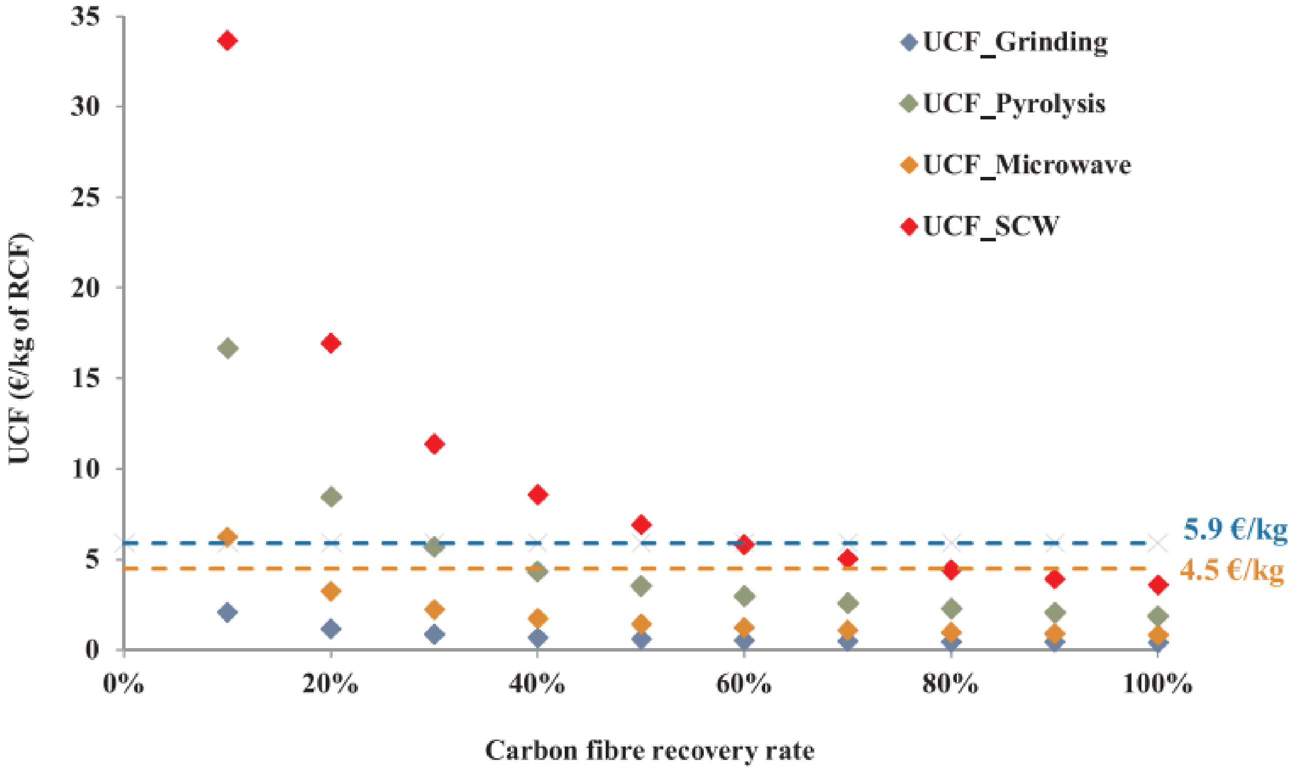


Figure 6-2: Sensitivity study of Economic Assessment by Carbon Fibre recovery rate [58]

Obviously, to an increase in recovery rate follows a decrease of the UCF, even if the highest is always represented by SCW. The range in which the prices are considered competitive to substitute v-CFs with r-CFs is the first between 0 and 4.5 €/kg (the minimum ideal cost that the industry aims to reach).

Similarly, the environmental assessment is performed by the previous authors, by means of the dedicated indicators:

- **Global Warming Potential (GWP)**: the extracted definition from the EPA is "The Global Warming Potential (GWP) was developed to allow comparisons of the global warming impacts of different gases. Specifically, it is a measure of how much energy the emissions of 1 ton of a gas will absorb over a given period of time, relative to the emissions of 1 ton of carbon dioxide (CO_2). The larger the GWP, the more that a given gas warms the Earth compared to CO_2 over that time period. The time period usually used for GWPs is 100 years" [68]. Since it is used as reference, CO_2 ha a unitary GWP. For instance, methane has an estimated GWP of 27-30, nitrous oxide has a GWP of 273 time of CO_2.
- **GWP impact of process (GWPP)**: accounts all the processes to manage the waste [58].
- **GWP impact of substituted products (GWPA)**: takes into account the GWP impacts from the utilisation of recovered products to replace v-CFs. The GWPA for an amount of recovered material is equal to GWP impacts of production of the same quantity of virgin products which the recovered products replace,
- **GWP total of the system (GWPTOT)**: includes impacts from both activities and susbstitution effect (Equation 11 from [58]).

$$GWPTOT = GWPP - GWPA \tag{11}$$

The contribution of these indicators can be appreciated in Figure 6-3 and 6-4, in which the GWP impact of each recycling method can be evaluated.

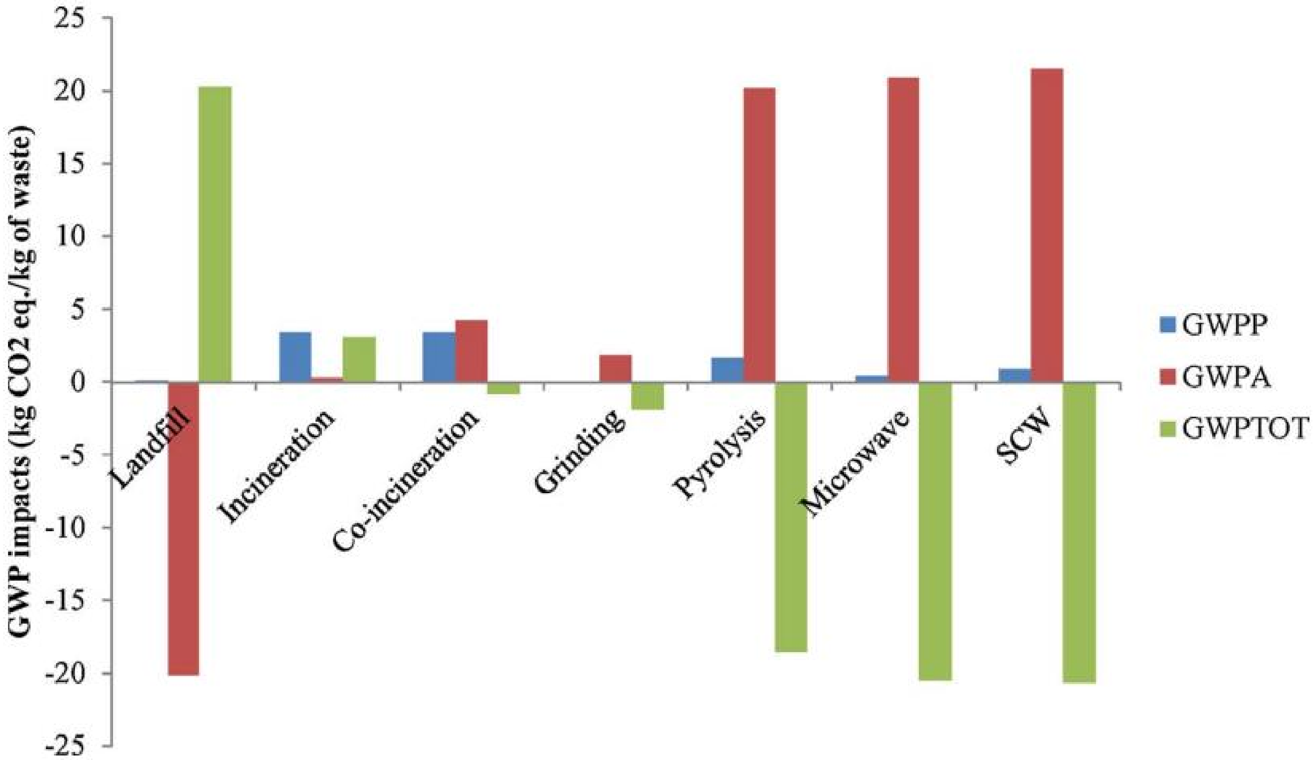


Figure 6-3: Environment assessment of the CFRP waste treatment techniques [58]

As it can be read from [70], the production of 1 kg of v-CFs requires 162 MJ of electrical energy and 191 MJ of heat from gas, leading to high production of green house gases (GHG), with a GWP impact of "31 $kg_{CO2,eq}$/kg" [69]. Thus, having a first look to Figure 6-3, the promotion of yield increase for r-CF seems clear. As for the GWPP impact, it can be seen that for each recycling process it is low enough to reach a negative GWPTOT. Nevertheless, the indicator of major interest is GWPA, which is pivotal for the understanding of the waste treatment and of which evaluation strictly depends on replaced material. Starting from landfilling, its low GWPP impact is compensated by the high GWPTOT, due to the absence of recycling potential of the CFs. Looking at the thermal processes, they show the highest values of GWPP. The highest among those three is represented by incineration, which involves the combustion of the entire composite. Then, in descending order, there is co-incineration in which the absence of ash landfilling induce a slightly lower impact. Therefore, a lower GWPP impact is reached in pyrolysis, where the combustion part of process induces to the decomposition of the polymeric matrix. However, in co-incineration, despite a high UCW (as can be seen in Figure 6-1), what makes it interesting is its GWPA, which is able to set a negative GWPTOT evaluation due to the recovery of CFRP waste on energy and material. As far as pyrolysis is concerned, GWP impact is low due to the high energy consumption, combustion of the matrix and absence of by-product recovery.

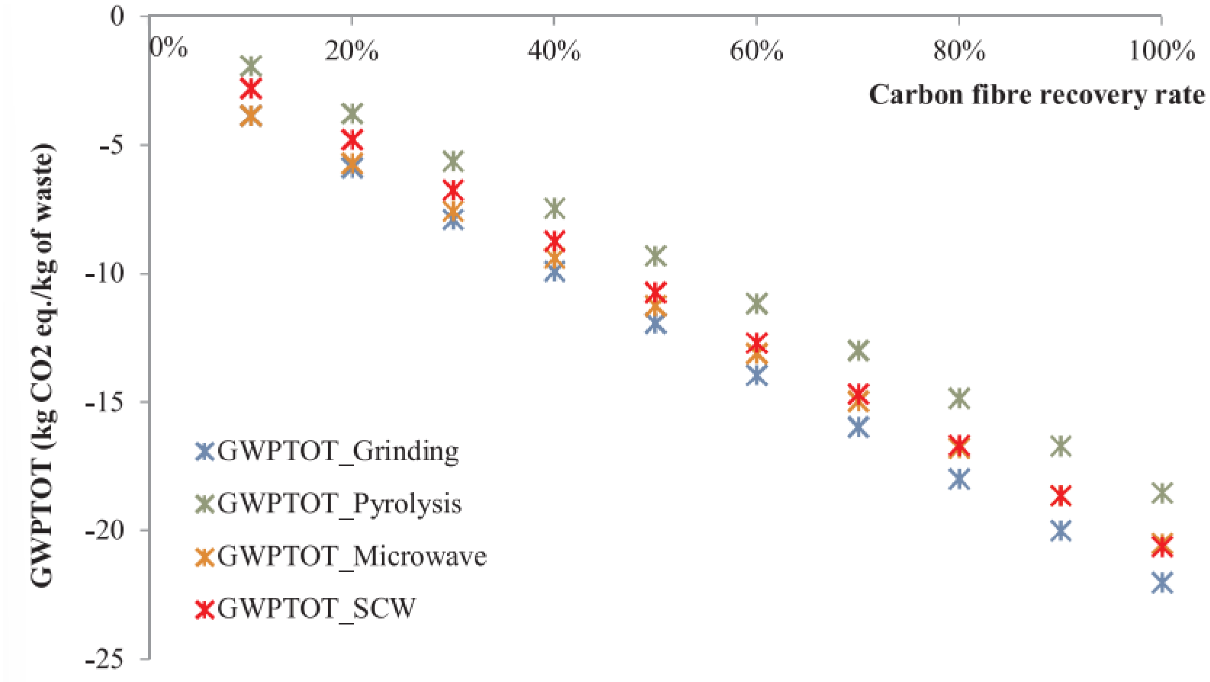


Figure 6-4: Sensitivity study of Environmental Assessment by Carbon Fibre recovery rate [58]

It has to be noticed that a pyrolysis process able to recover the condensable degrade polymeric matrix from incomplete oxidation, can decrease the GWPTOT leading to values comparable with microwave and SCW. Then, mechanical recycling is the most eco-friendly process, but the use of fibers at high yield is not so easy due to the degradation of the fiber properties. In fact, in GWPA assessment, the effect of low-value application can be recognized, making this process the least interesting one. However, the highest GWPTOT (in negative) are reached by microwave and SCW, in which the recovery of by-product (oligomers) represents a key factor. The gap in GWPP between microwave and SCW is compensated by the oligomers yield release, which is higher in SCW.

Thanks to a research performed by Vong et al. [58], the economic and GWP assessments show these main outcomes:

- Landfill and incineration represent the cheapest way for the waste disposal, but inducing to high GWP impacts because of the loss of recovered materials.
- Recycling techniques with high yield of recovery claim more capital (such as SCW), allowing, instead, important reduction in GHG emission and leading to a consistent reduction of GWP.

The main problem, however, is represented by the fact that each recycling process cannot achieve either low cost or GWP impacts. In case further information are needed, refer to the paper referenced in [58].

To conclude, four of the most famous companies that deal with the r-CFs are listed in Table 6-4.

Table 6-4: Companies that deals with r-CFs (handmade)

RYMYC	Italian industry, have focused R&D in the removal of epoxy resins, binders, sizing and coating from carbon fibre composite waste, and have installed a textile plant of 500 t/year capacity suitable to transform the recycled carbon fibre into nonwoven to be used again in carbon fibre composite market, creating a circular economy. They produce "RYMFELT", "RYMPLATE" and "RYMCUT", which are good and high-quality composite materials. [80]
RECARBON	Another Italian industry, which has developed functional approach for manufacturing CFRPs from r-CFs. Their products are "Organosheets - OS" (r-CFs and thermoplastic polymers according to customer needs and processed to produce flat panels) and "Prepregs" (CFRPs with r-CFs to form strong yet lightweight components). [81]
GEN2CARBON	Focused on the delivery of next generation carbon fibre recovery systems and the expansion of recycled nonwoven technologies. Also aimed at reducing their environmental impact from production to EoL of their products. Their products are "G-TEX M", a 100% recycled carbon fibre fabric and "G-TEX TM", a thermoplastic and recycled carbon fibre hybrid blend. [82]
MANIFICA	The global ambition of MANIFICA is to set up the recycling chain of carbon fibre composites "from aeronautic waste to innovative composite parts". The vision of MANIFICA is that high-quality recycled carbon fibres (r-CFs) will drive the recycling industry towards economic value. A range of semi-products with a thermoplastic matrix is being studied for automated process (AFP, FRT). All the semi-products are made of aeronautical quality carbon fibres (standard modulus or intermediate modulus). [83]

7. Energy insights

In this last chapter a brief analysis is being carried out from one of the above-mentioned techniques, namely pyrolysis. As said before, the topic on recycling techniques suffers from exhaustive information, as it is not yet industrially mature and viable. Hence, the evaluations performed in this chapter have been realised without unrealistic assumptions.

Obviously, it comes easy to wonder why this technique has been chosen among the others. This selection has been decided because of multiple advantages and not only considering the CFs reclamation. In fact, the outcomes of this process are not only the r-CFs, but also both condensed vapour and gaseous fractions, which can be recovered and reused in whatever form, also helping in avoiding several pollutant emissions and decreasing the GWPTOT (see Chapter 6).

The main aim of this search is to understand if something can be recovered from the pyrolysis gaseous product in terms of heating value, by producing fuel-gas from polymeric matrix. It would be really pitiful not to consider the embodied energy in the gaseous fraction, which could be useful in many different ways (partially sustaining the process, producing H_2, collecting and selling it and so on).

This section has been written by taking as cornerstone two papers:

- The first paper, written by "Y. Kodera et al." [71], is based on a feasibility study conducted on fuel-gas production from plastic waste, performed on a bench-scale pyrolysis reactor and scaling up the dimensions for a reactor able to treat higher capacity. This paper gives useful information since it is essentially the only one that shows a complete and detailed guide on mass and energy balances.
- The other one, written by "A. Lopez-Urionabarrenechea et al." [72], practically represents the focus of this section and treats the H_2 production starting from the pyrolysis of CFRPs aimed at carbon fibers reclamation.

7.1.1 Guideline to perform an energy balance on a pyrolysis reactor

Unfortunately, due to the lack of sufficient information, it has not been possible to realize a proper and detailed energy balance. However, the guideline offered by Kodera et al. [71] deserves to be mentioned as well. In short, the research has been conducted on fuel-gas production from plastic waste using an externally heated rotary kiln.

In particular, the reactor is externally heated by an LPG burner and is composed by a retort (rotating reactor), heating-gas chamber and a casing (Figure 7-1). The hot gases coming from the generator heat up the chamber passing outside through the retort and then leave the reactor through a chimney. Since the focus of this sub-paragraph is the energy balance, further information can be found in the cited paper.

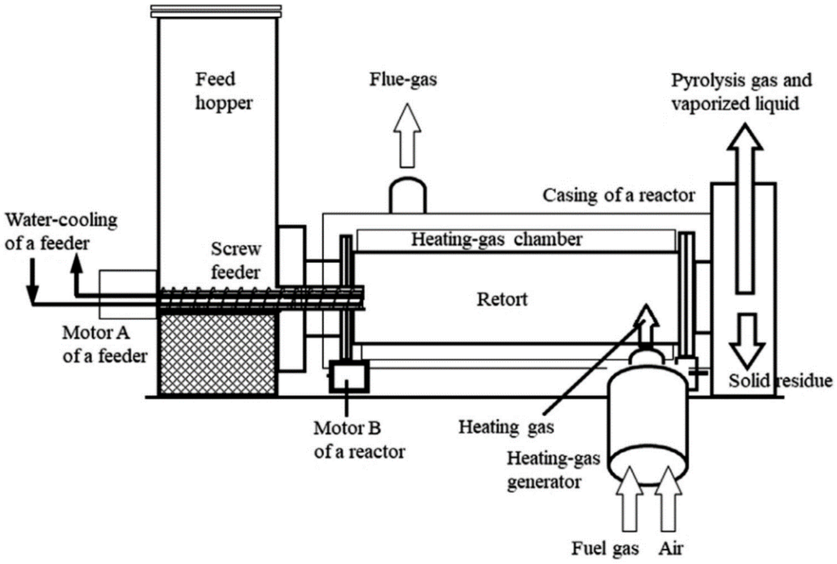


Figure 7-1: Schematic of core part of pyrolysis plant [71]

Therefore, burning LPG using air produces heating gas, of which aim is to pyrolyze the polymeric waste inside the reactor at around 650°C. The products leave the reactor with some sensible heat, while another portion of the products absorbs latent heat during melting/evaporation. In order to build up the energy balance, some basic steps should be followed, taking into account the diagram in Figure 7-2.

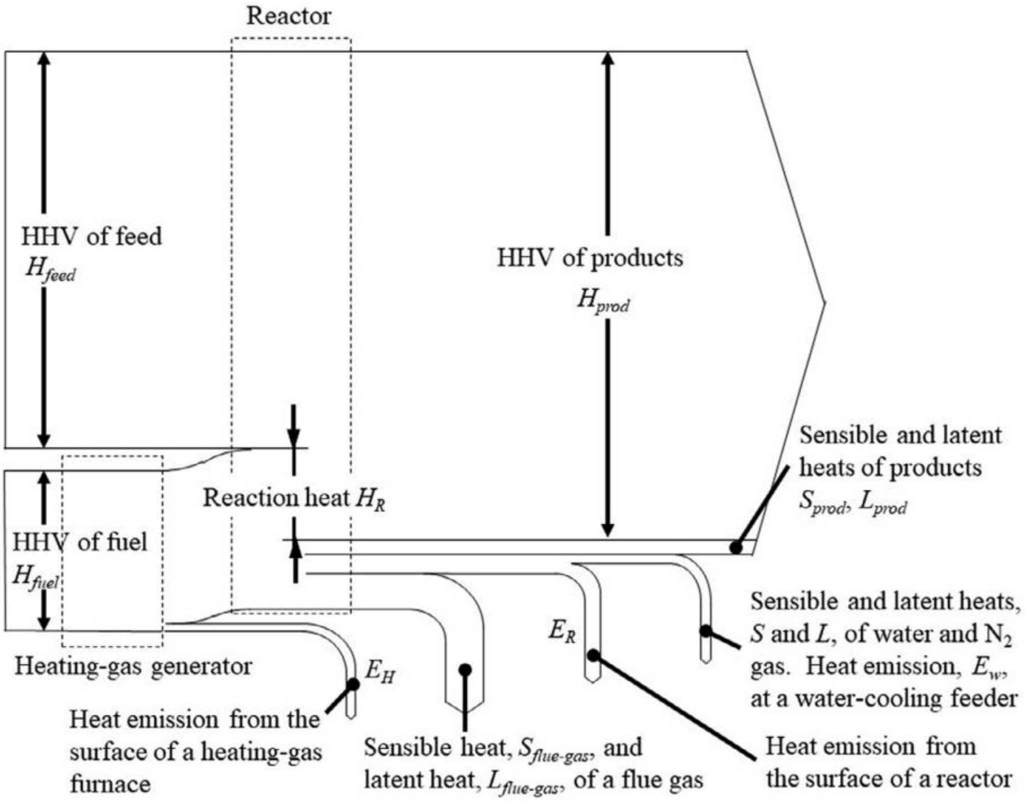


Figure 7-2: Heat flow diagram [71]

Starting from the heat supplied from the burner "H_{fuel}", it is possible to understand that some contributions in heat terms are lost as: heat emission of the generator "E_H", heat emission of the reactor "E_R", heat emission at water-cooling feeder "E_W", heat consumed at the reactor and the remaining part discharged as sensible and latent heat of flue-gases ($S_{flue\text{-}gas} + L_{flue\text{-}gas}$), other sensible and latent heat contributions of nitrogen N_2 and of the products ($S_{products}$ and $L_{products}$). All of these contributions have to be calculated in order to evaluate the other flows. Furthermore, the reaction heat "H_R" is supplied by means of the heat consumed at the reactor and transferred through the surface. Once the total HHV of the polymeric waste at the input "H_{feed}" and of the products at the output "H_{prod}" are known, it is possible to evaluate the reaction heat as the difference between them. Then, the heat transfer across the reactor's wall is given by the following formula in Equation 11 (and will be used for the further calculation performed in the analysis of the next paragraph):

$$Q_{loss} = U \cdot A \cdot \Delta T_m \ [W] \tag{11}$$

In Equation 11 "U" is the overall heat-transfer coefficient, "A" is the heat transfer area and "ΔT_m" is the logarithmic mean temperature of the retort. At the end, the total heat input should match the total heat output in the plant operation. Nevertheless, if the main aim is to produce fuel-gas, the total calorific values of the product (gaseous and liquid) must be higher than the overall energy consumption (accounting also the energy spent as electricity). Then, the energy efficiency of pyrolysis is evaluated by means of Equation 12:

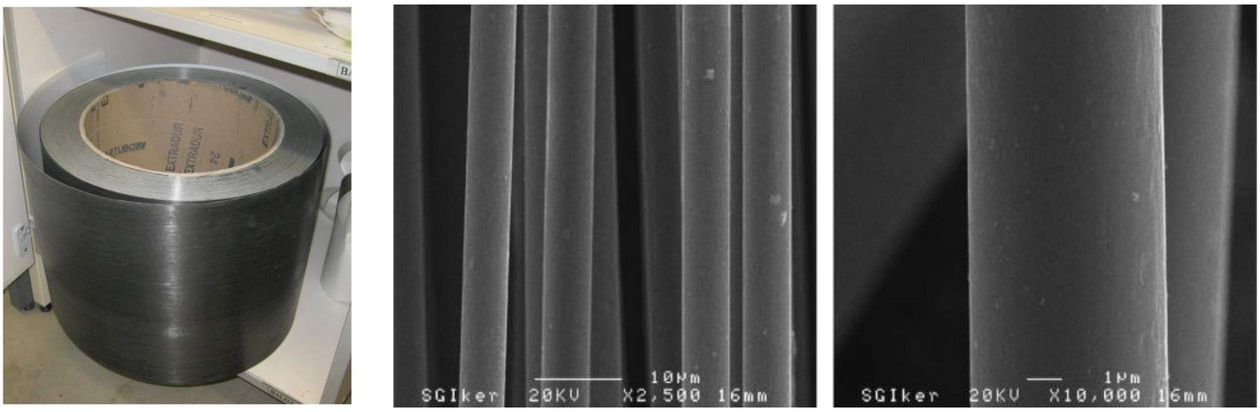
$$\eta = \frac{H_{prod}}{H_{feed} + H_{fuel}} \cdot 100 \ [\%] \tag{12}$$

7.2 Valorisation of gases from CFRPs pyrolysis

As said before, it would be limiting if only the CFs were considered as outcomes of the process. In fact, the products coming from the polymeric matrix should be valorised in some way. Once the CFRP is pyrolyzed, the cooling down of volatile matter produces liquids and will leave the remaining portion of the products as gases. However, depending on the polymeric matrix composition, the condensed liquid will be a two-phase mixture solved in water and oily fraction. Therefore, the recovery of this complex mixture would not be neither feasible nor convenient.

The gaseous fraction is generally composed of gases such as methane CH_4, carbon dioxide CO_2, carbon monoxide CO, hydrogen H_2 and hydrocarbons in small parts. Hence, this gaseous mixture can have multiple application from saving energy in the same process to be sold or applied at industrial level. This is even more true if the gaseous fraction is rich in H_2 content, remembering that the LHV of hydrogen is equal to "119.96 MJ/kg @ 25°C" [73]. This is only one of the multiple benefits coming from the hydrogen application. An entire digression can be opened on this subject, as since it is not the main topic the reader is suggested to visit the IEA publication on "The future of Hydrogen" [74].

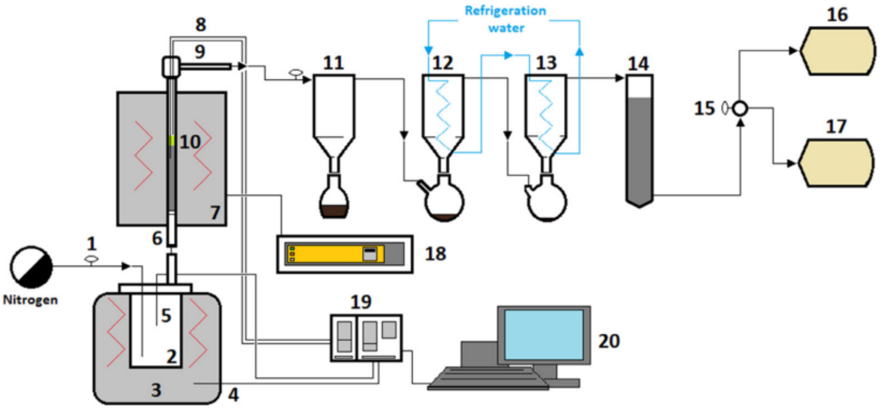
On this purpose, some rough calculations (in the attached Excel worksheet) have been performed in order to verify the energy content of the gaseous products and ensuring the quality of r-CFs (Figure 7-3b). The main work on which the evaluations are based is the one conducted by the author of [72].



(a) (b)

Figure 7-3: M21 carbon fiber pre-preg roll [75]

The pyrolyzed composite (Figure 7-3a) is composed by 34 wt% of "M21 epoxy resin (Hexcel)" and 66 wt% of "T800S unidirectional carbon fibers (Toray)". For further information inherent to its physical and chemical properties see the referenced paper [75]. The operative conditions chosen to approach the proper evaluations have been extracted mainly from [72], few from [71], and listed in the rearranged Table 7-1. Then, the experimental set-up adopted by the authors of [72] is showed in Figure 7-4.



1	Rotameter	11	Condenser 1
2	Pyrolysis / oxidation reactor	12	Condenser 2
3	Pyrolysis / oxidation furnace	13	Condenser 3
4	Furnace thermocouple	14	Activated carbon column
5	Reactor thermocouple	15	T valve
6	Tubular reactor	16	Gas bag 1
7	Tubular furnace	17	Gas bag 2
8	Tubular reactor thermocouple	18	Tubular furnace temperature-control
9	Vapor and gas outlet	19	Pyrolysis / oxidation furnace temperature-control
10	Solid bed material	20	Computer

Figure 7-4: Pyrolysis lab-scale installation [72]

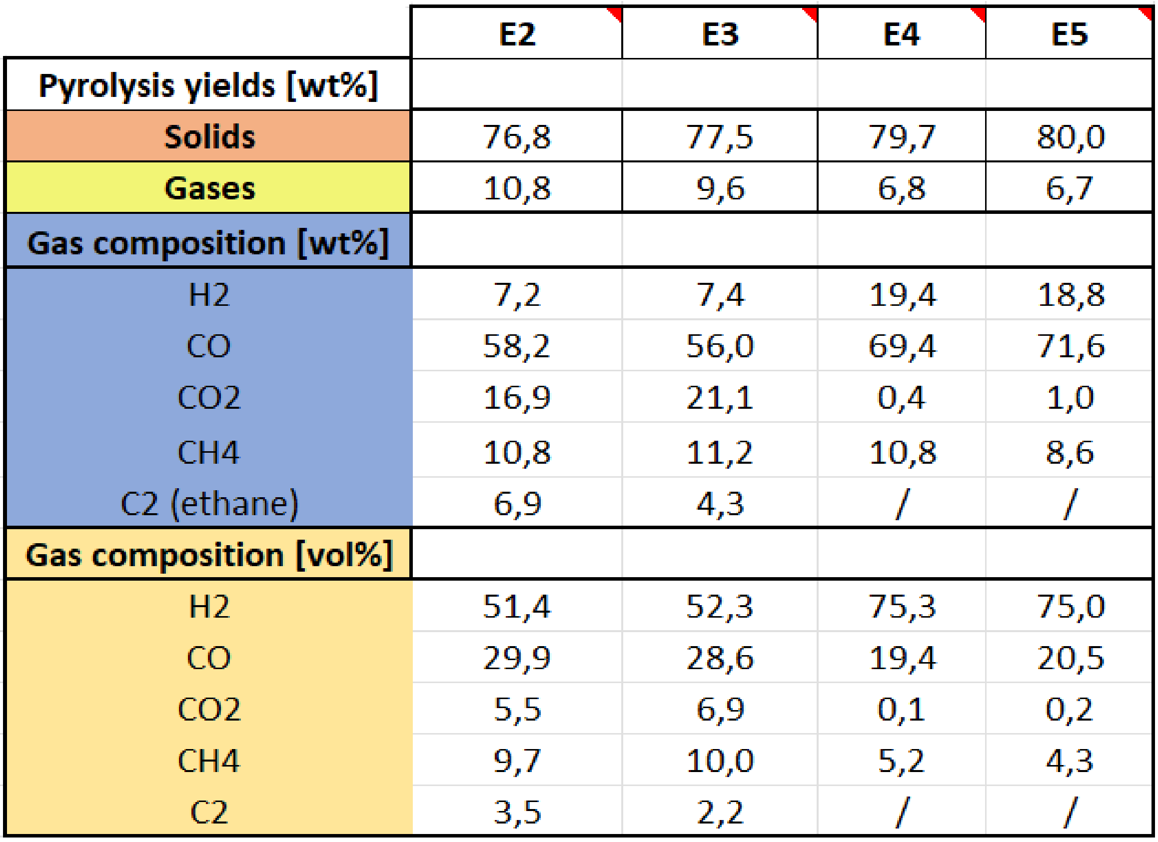
In this case, the reactors are heated-up by means of an electric furnace and not by a burner, as in the rotary kiln in [71]. In each experiment, 100 g of waste CFRP are introduced as single sheet and heated up to 500°C at 3°C/min and then oxidized at the optimized condition of 500°C for 165 min (to reach the solid remaining fraction to a level equal to 66 wt%). Therefore, the outcomes from the first reactor flow to the second one undergoing to 900°C for severe cracking reactions. The volatile matter (vapours and gases) are cooled down passing thorugh three condensers (two air-cooled and one water-cooled). The condensable vapors are collected as liquids, while the gaseous fraction is cleaned by means of activated carbon column and collected in bags.

Table 7-1: Data for pyrolysis process [71], [72]

Pyrolysis temperature [72]	500 °C
Heating rate [72]	3 °C/min
Pyrolysis time [72]	30 min
Reactor room temperature [71]	34,5 °C
Mass of CFRP sample per experiment [72]	0,1 kg

As for the outcomes of the process, referring to the cited paper [72], four different runs have been performed with different conditions, and the results are listed in Table 7-2 (extracted from [72] and rearranged).

Table 7-2: Results of the experiment [72]



	E2	**E3**	**E4**	**E5**
Pyrolysis yields [wt%]				
Solids	76,8	77,5	79,7	80,0
Gases	10,8	9,6	6,8	6,7
Gas composition [wt%]				
H2	7,2	7,4	19,4	18,8
CO	58,2	56,0	69,4	71,6
CO2	16,9	21,1	0,4	1,0
CH4	10,8	11,2	10,8	8,6
C2 (ethane)	6,9	4,3	/	/
Gas composition [vol%]				
H2	51,4	52,3	75,3	75,0
CO	29,9	28,6	19,4	20,5
CO2	5,5	6,9	0,1	0,2
CH4	9,7	10,0	5,2	4,3
C2	3,5	2,2	/	/

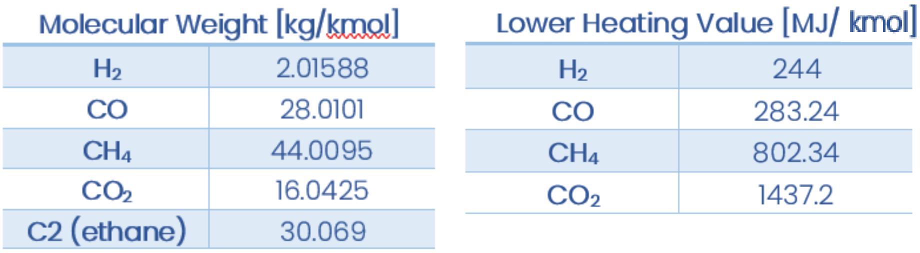
The different experiments are carried with different specifications [72]:

- E2 – experiment realised with the solid bed of tubular reactor made of residual refractory material instead of SiC .
- E3 – experiment carried with the same conditions of the previous one but without dwelling at the end of pyrolysis process.
- E4 – experiment carried using N_2 only to purge the reactors before starting the process. No additional inert gas is injected once all the air is removed from the reactor.
- E5 – experiment carried without using N_2 as inert reaction medium. Reactor filled with just natural air.

Looking at Table 7-2, it seems clear that each consecutive experiment is aimed at increasing the hydrogen concentration inside the gases. As the authors said, "the results obtained in the last two experiments are very relevant, even more in the last one taking into account that in this case N_2 is not used in the whole process. In short, in view of the experiments carried out, it can be concluded that it is possible to obtain a gaseous fraction with a high percentage of hydrogen through a thermal treatment process without consumption of N_2 and using a residual material as filler. At the same time, a liquid product composed mainly of water is generated. Now, the future approach would consist on separating the H_2 from the gases by pressure swing adsorption (PSA). This would generate high purity H_2" [72]. In fact, in the last two experiments, at least half of the hydrogen contained in the polymeric resin is recovered in the form of bi-atomic hydrogen. However, as far as each experiment is concerned, the gaseous fractions are mainly composed of CO, with good concentrations of hydrogen and methane, while few amounts of CO_2 are measured, and the ethane content is almost negligible. As for the solids, the difference between the resulting fractions and the 66 wt% is equal to the char deposited on the fibers, which has to be removed by means of the oxidation step.

Therefore, having the products composition on percentage, it has been possible to go on with further calculation aimed at the evaluation of the CFRPs' Lower Heating Value. In Table 7-3 the LHV of each gaseous fraction constituent and their molecular weight are listed.

Table 7-3: Molecular Weight and LHV of gases [76]



Molecular Weight [kg/kmol]	
H_2	2.01588
CO	28.0101
CH_4	44.0095
CO_2	16.0425
C2 (ethane)	30.069

Lower Heating Value [MJ/ kmol]	
H_2	244
CO	283.24
CH_4	802.34
CO_2	1437.2

Then, using the rule of mixtures (Equation 13), it has been possible to evaluate the Syngas LHV (results in Table 7-4):

$$LHV_{syn} = \sum_i \left(\frac{LHV_i}{MM_i} \cdot wt\%_i\right) \qquad (13)$$

In Equation 13 LHV_i, MM_i, $wt\%_i$ is respectively the lower heating value, the molecular weight and the weight composition in percentage of each component.

Table 7-4: LHV of the obtained gaseous fraction (handmade)

Syngas Lower Heating Values LHV [MJ/kg]			
E2	**E3**	**E4**	**E5**
23,30	22,28	**35,90**	**34,30**

Not surprisingly, thanks to the increased concentration of hydrogen, the LHVs of the gases obtained in the last two experiments are good enough to consider them "useful". However, these values should be at least higher than the LHV of the CFRP at the inlet of the reactor. In order to evaluate the HHV and LHV of the CFRP composite in question, the proximate and the ultimate analyses obtained in the experiments (Table 7-5) can be useful.

Table 7-5: Proximate and Ultimate analyses for each experiment [72]

	CFRP @ in.	**E2**	**E3**	**E4**	**E5**
Proximate Analysis [wt%]					
Moisture	0,3	0,4	0,4	0,1	0,3
Volatiles	29,7	6	5,9	6,4	6,6
Fixed Carbon	69,4	93,3	93,4	92,9	92,8
Ash	0,6	0,3	0,3	0,6	0,3
Ultimate Analysis [wt%]					
C	85,4	95,5	95,6	96,1	96,2
H	2,7	<0,1	<0,1	<0,1	0,1
N	4,5	3,4	3,6	3,6	3,5
S	1,6	<0,1	<0,1	<0,1	<0,1
Others	4,9	1,1	0,8	0,3	0,2

On the basis of the Ultimate Analysis, it is possible to evaluate the HHV of the CFRP at the inlet of the reactor and the values of the solid products at the end of the experiments to compare the initial and the final solid sample. This can be done thanks to the correlation in Equation 14 [77]:

$$HHV = (33.5[C] + 142.3[C] - 15.4[C] - 14.5[C]) \cdot 10^{-2} \left[\frac{MJ}{kg}\right] \tag{14}$$

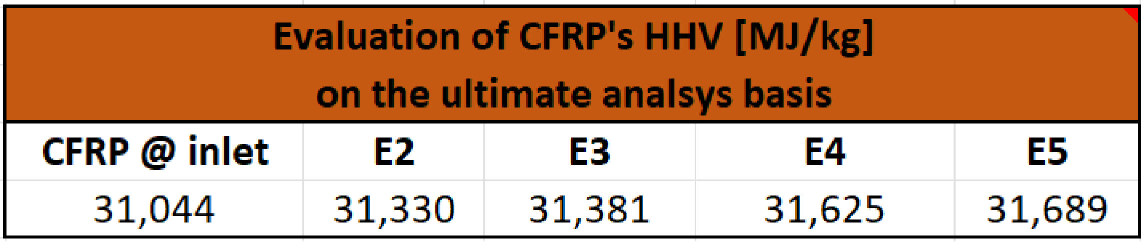
In this evaluation, the weight percentage lower than 0.1% are considered to be negligibile. Therefore, once the HHV is evaluated, thanks to another correlation (Equation 15 [77]), it is possible to calculate the LHV:

$$LHV = HHV \cdot \left(1 - {}^{MC_{WB}}/_{100}\right) - 2.447 \cdot \left[MC_{WB} + H \cdot 9.01 \cdot \left(1 - {}^{MC_{WB}}/_{100}\right)\right] \cdot 10^{-2} \left[\frac{MJ}{kg}\right] \tag{15}$$

In which MC_{WB} corresponds to the initial content of humidity (assumed to be null) and H is the hydrogen content on dry basis.

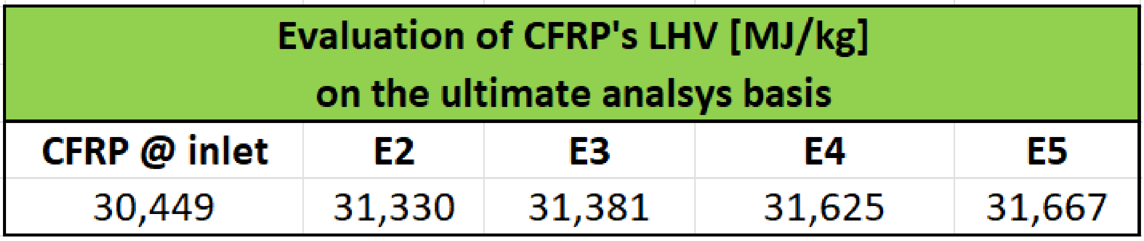
Thanks to Equation 14 and Equation 15, the results have been obtained and listed in Table 7-6 and Table 7-7.

Table 7-6: CFRPs and solid products HHVs (handmade)



Evaluation of CFRP's HHV [MJ/kg] on the ultimate analsys basis				
CFRP @ inlet	**E2**	**E3**	**E4**	**E5**
31,044	31,330	31,381	31,625	31,689

Table 7-7: CFRPs and solid products LHVs (handmade)



Evaluation of CFRP's LHV [MJ/kg] on the ultimate analsys basis				
CFRP @ inlet	**E2**	**E3**	**E4**	**E5**
30,449	31,330	31,381	31,625	31,667

Looking at the results above, it is possible to appreciate that the LHV of the gaseous products is slightly higher than the one of the CFRP at the inlet of the reactor, so it is possible to state that the syngas obtained from the polymeric matrix have a not negligible value.

Once these figures are obtained, the reader can wonder if the process can be self-sustainable or at least if allows to recover energy and costs. In order to answer to this question, some other figures have to be evaluated.

Due to poor and inaccurate information, the figures which represent the main heat flows during the experiment are evaluated by means of the available sources. Starting from the heat required to heat-up the composite during the pyrolysis step, its specific heat has been evaluated thanks to the relationship found in Figure 7-5 [78].

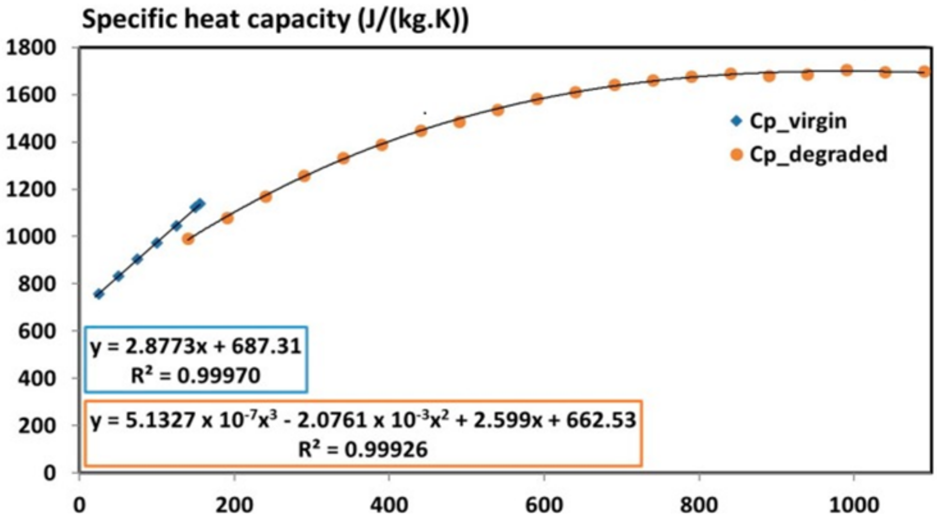


Figure 7-5: Specific heat capacity of CFRP composite [78]

Therefore, by means of Equation 16 the required heat has been calculated:

$$Q_{py} = m \cdot c_p \cdot \Delta T \quad [J] \tag{16}$$

In this report it is not specified how this heat is provided to the material, it can be done applying electric furnaces like in [72] or also external burner as in [71].

As for the heat losses, Equation 11 has been applied following the guideline given by [71]. It must be said that the authors in [72] have used silicon carbide (SiC) and a high alumina refractory material inside the tubular reactor but, unfortunately, did not report the thermal properties required to perform a good analysis on heat losses, which would certainly have led to more promising results. Therefore, since precise data are showed in [71] and since the gaseous composition is not a function of the reactor's dimensions, the rotary kiln used by the authors in [71] has been chosen to perform the evaluations (diameter of 0.216 m with a length of 1 m). Hence, the lateral surface of the reactor has been evaluated thanks to Equation 17 in which D is the diameter and L the length:

$$A_{lat} = \pi \cdot \frac{D}{2} \cdot L \quad [m^2] \tag{16}$$

The paper shows a value of the overall heat-transfer coefficient "U" equal to 40 W/(m^{2}K), while for simplicity and due to absence of precise values, a normal difference is used instead of the logarithmic mean value of the temperatures.

Another important figure that misses is the enthalpy of reaction of the material. Again, a lack of information about this value for CFRPs occurs, so on the basis of [79] a strong assumption has been done. In according to the enthalpy of pyrolysis of the polymeric material that ranges between "205 and 209 J/g" [79], the one of CFRPs is for sure in the same order of magnitude (assumption done looking at the various referenced papers). Hence, values around 700 J/g have been used to perform the analysis, since they can represent a realistic and solid assumption.

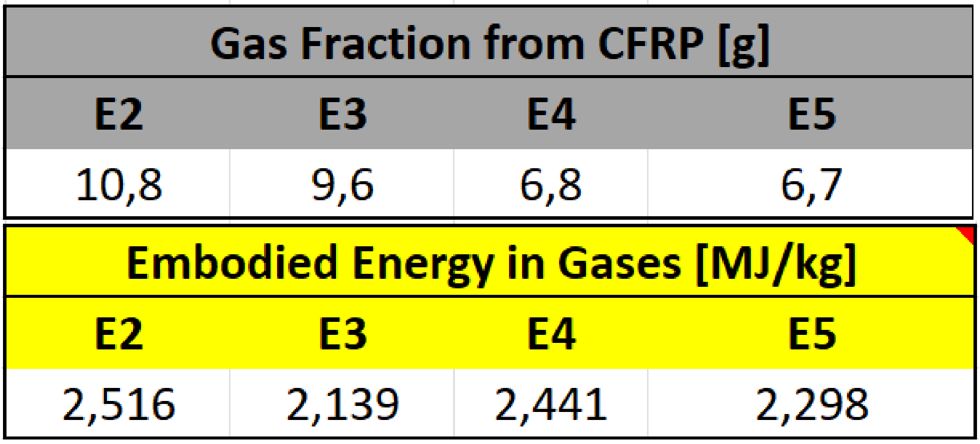
Therefore, the results and the sum of these contributions are listed in Table 7-8.

Table 7-8: Energy contribution relative to the CFRP pyrolysis (handmade)

Energy required to heat-up the CFRP [MJ/kg]	0.777
Heat losses at the reactor [MJ/kg]	113.717
Enthalpy of pyrolysis [MJ/kg]	0.700
Total energy required for pyrolysis [MJ/kg]	115.294

In Table 7-9 the energy contained in the gaseous fraction of the products are showed in order to give a basis for comparison, taking into account the gases wt% and their LHV.

Table 7-9: Weight percentage and energy of the pyrolysis gases (handmade)



Gas Fraction from CFRP [g]			
E2	E3	E4	E5
10,8	9,6	6,8	6,7

Embodied Energy in Gases [MJ/kg]			
E2	E3	E4	E5
2,516	2,139	2,441	2,298

It seems clear that the worst contribution is represented by the heat losses, that set the contribution of the recovered energy embodied in the gas almost useless. In order to reduce the losses, direct actions aimed at the reduction of the heat-transfer coefficient can be applied, such as using better material or properly sizing the reactor (e.g., standing on what has been said about the paper [72], if proper evaluations have been realized on the basis of that reactor, the figure of heat losses would be much smaller setting the recovered gaseous fraction more valuable).

In conclusion, this rough analysis has been realized just to give a fundamental basis to the reader who is interested in realizing a "greener" process, since it is true that in this case the recovered energy is two orders of magnitude lower than the one spent for the process. However, it is always a cleaner type of energy that could be used to partially supply energy to the process (even better with further optimization of the process to produce pure H_2) or to be sold as chemical gaseous by-product. Nevertheless, it should be remembered that, thanks to this process, not only high-quality r-CFs are reclaimed, but also the polymeric matrix is consistently valorised in form of H_2 (way much eco-friendlier and better compared to the combustion of the whole gaseous fraction).

8. Conclusions

In this thesis, the reader can appreciate a deep understanding of a topic that, to date, is poorly treated if not only for reclamation of products that have yet to be optimized in the near future. In fact, by means of this report the fundamental and working aspects of the CFRP recycling techniques are thoroughly described and analyzed, and also the different mechanical, thermal and chemical recycling methods are consolidated.

The collected literature and a more understanding of the topic have led to the conclusion that the recycling process has to be chosen in function of the CFRP type and the field in which the recovered product is used.

Specific pros and cons of each method have been highlighted as well. Mechanical recycling is suitable for CFRPs but with further optimization to be accounted, while chemical and thermal recycling allow to obtain long fibers with excellent retention of mechanical properties but, because of chemicals by-products and solvents, non-negligible impact on the environment and ecosystem is created, and more energy is consumed due to the high required operative temperatures. In general, pyrolysis and solvolysis are the best techniques among the others for the recycling/recovery of the CFs as offer high-quality and high-valuable r-CFs. Nevertheless, mechanical and pyrolysis processing (even if coupled together) show better potential to be used at industry scale applications, since they are able to dispose higher capacities of waste composites. However, researchers are still working on ensuring the properties of r-CFs as closer as possible to the ones of the v-CFs. In the main, in order to evaluate all the environmental and economic viabilities of these methods, accurate approached need to be established to help decision makers in having a comprehensive understanding on the applicability, cost, and environmental benefit of recycled components.

In the near future, the recycling of CFs will play a significant role in establishing a circular economy approach for these high-quality fibers, and this is why further research are required to improve the quality of CFs and decreasing environmental impact of these methods.

References

[1]. "Energy use per person, 2021." https://ourworldindata.org/grapher/per-capita-energy-use?time=latest (accessed Sep. 02, 2022).

[2]. B. Gates, "How to avoid a climate disaster: the solution we have and the breakthroughs we need." 2021.

[3]. "Earth Overshoot Day 2022 Home - #MoveTheDate". https://www.overshootday.org/ (accessed Sep. 02, 2022).

[4]. "151 Inspiring Environmental Quotes About Global Warming, Climate Change and Sustainability – Mahatma Gandhi". https://www.conserve-energy-future.com/inspiring-environmental-quotes.php (accessed Sep. 02, 2022).

[5]. "CO_2 and Greenhouse Gas Emissions - Our World in Data." https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions (accessed Sep. 02, 2022).

[6]. IEA (2021), World Energy Outlook 2021, IEA, Paris https://www.iea.org/reports/world-energy-outlook-2021.

[7]. "Emissions by sector – Our World in Data." https://ourworldindata.org/emissions-by-sector (accessed Sep. 02, 2022).

[8]. "bp Statistical Review of World Energy 2022, 71th edition." https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2022-full-report.pdf.

[9]. "Building confidence in recycling carbon fiber". https://www.compositesworld.com/articles/building-confidence-in-recycled-carbon-fiber (accessed Aug. 17, 2022).

[10]. Namazi H. (2017). Polymers in our daily life. BioImpacts : BI, 7(2), 73–74. https://doi.org/10.15171/bi.2017.09.

[11]. "Why are polymers useful?" https://trp.co.uk/why-are-polymers-useful/ (accessed Apr. 12, 2022).

[12]. Dorel Feldman (2008) Polymer History, Designed Monomers and Polymers, 11:1, 1-15, https://doi.org/10.1163/156855508X292383.

[13]. "Plastics – the Facts 2021." https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/ (accessed Apr. 12, 2022).

[14]. "Polymer – Wikipedia." https://en.wikipedia.org/wiki/Polymer (accessed Apr. 12, 2022).

[15]. "Examples of Natural Polymers and Their Monomers – Science Notes." https://sciencenotes.org/examples-of-natural-polymers-and-their-monomers/ (accessed Apr. 12, 2022).

[16]. "Explainers: What are Polymers? – Science News for Students." https://www.snexplores.org/article/explainer-what-are-polymers (accessed Apr. 12, 2022)

[17]. Ferraris M. "Slides from the course Advanced Materials for energy applications, MSc in Energy and nuclear engineering (PoliTo)". Torino. And related references.

[18]. Callister W.D., Materials science and engineering: an introduction, John Wiley & Sons, Inc, 2007, 7th edition.

[19]. "Thermosets Vs. Thermoplastics - Romeo RIM." https://romeorim.com/thermoset-vs-thermoplastics/ (accessed Apr. 12, 2022).

[20]. "Thermoplastics vs. Thermosetting Polymers: Properties, Processing and Applications – Matmatch." https://matmatch.com/learn/material/thermoplastics-vs-thermosetting-polymers (accessed Apr. 12, 2022).

[21]. "Materials Science & Engineering -UNSW Sydney." https://www.materials.unsw.edu.au/study-us/high-school-students-and-teachers/online-tutorials/polymers/forming-methods (accessed Apr. 12, 2022).

[22]. "5 Types Of Plastic Moulding – Active Plastics." https://www.activeplastics.co.nz/types-of-plastic-moulding (accessed Apr. 14, 2022).

[23]. "Blow Molding – Plastic Technologies, Inc." https://www.plastictechnologiesinc.com/Blow%20Molding.html (accessed Apr. 12, 2022).

[24]. "Importance of Distance Parameter in Plastic Molding Design – A.C.E." https://www.ace-mold.com/importance-of-distance-parameter-in-plastic-molding-design/ (accessed Apr. 14, 2022).

[25]. "Rotational Molding – IQS Directory." https://www.iqsdirectory.com/articles/rotationally-molded-plastic/rotational-molding.html (accessed Apr. 14, 2022).

[26]. "A primer on six methods for forming plastics – Plastics Today" https://www.plasticstoday.com/injection-molding/primer-six-methods-forming-plastics (accessed Apr. 14, 2022).

[27]. "An overview of Reaction Injection Molding – Makenica Inc." https://makenica.com/an-overview-of-reaction-injection-molding/ (accessed Apr. 14, 2022).

[28]. "Plastic Manufacturing – "Warren Design and Technology." https://www.the-warren.org/GCSERevision/engineering/plastic%20forming.htm (accessed Apr. 14, 2022).

[29]. Balani, K., Verma, V., Agarwal, A. and Narayan, R. (2014). Physical, Thermal, and Mechanical Properties of Polymers. In Biosurfaces (eds K. Balani, V. Verma, A. Agarwal and R. Narayan). https://doi.org/10.1002/9781118950623.app1

[30]. "Flory-Fox Equation – Wikipedia." https://en.wikipedia.org/wiki/Flory%E2%80%93Fox_equation (accessed Apr. 17, 2022).

[31]. Arya, R.K.; Thapliyal, D.; Sharma, J.; Verros, G.D. Glassy Polymers—Diffusion, Sorption, Ageing and Applications. Coatings 2021, 11, 1049. https://doi.org/10.3390/coatings11091049

[32]. "Crystallization of polymers – Wikipedia." https://en.wikipedia.org/wiki/Crystallization_of_polymers#:~:text=Examples%20of%20semi%2Dcrystalline%20polymers,or%20isotactic%20polypropylene%20(PP). (accessed Apr. 17, 2022).

[33]. "ISO 6603-2:2000(en) – Online Browsing Platform." https://www.iso.org/obp/ui/#iso:std:iso:6603:-2:ed-2:v1:en (accessed Apr. 20, 2022).

[34]. "Ductile / Brittle Transition Temperature – Omnexus." https://omnexus.specialchem.com/polymer-properties/properties/ductile-brittle-transition-temperature (accessed Apr. 23, 2022).

[35]. "Elastomers – Polymer Database." https://polymerdatabase.com/Elastomers/Elastomers.html (accessed Apr. 23, 2022).

[36]. Bhatt P, Goe A. Carbon Fibres: Production, Properties and Potential Use. Mat.Sci.Res.India;14(1). Available from: http://www.materialsciencejournal.org/?p=5641

[37]. "Carbon Fibers – Wikipedia." https://en.wikipedia.org/wiki/Carbon_fibers (accessed Mar. 2, 2022).

[38]. "Carbon Fiber – Material Strategies." https://arch5541.wordpress.com/2012/10/26/carbon-fiber/ (accessed Mar. 2, 2022).

[39]. Ton Peijs, Robert Kirschbaum, Pieter Jan Lemstra, A critical review of carbon fiber and related products from an industrial perspective, Advanced Industrial and Engineering Polymer Research, 2022, ISSN 2542-5048, https://doi.org/10.1016/j.aiepr.2022.03.008

[40]. "Carbon Fibers and Carbon Fiber-Reinforced Plastic (CFRP) – sgl carbon." https://www.sglcarbon.com/en/carbon-fibers-and-cfrp/ (accessed Mar. 2, 2022).

[41]. Peebles, L.H. (1995). Carbon Fibers: Formation, Structure, and Properties (1st ed.). CRC Press. https://doi-org.ezproxy.biblio.polito.it/10.1201/9781351070423

[42]. Huang X. (2009). Fabrication and Properties of Carbon Fibers. Materials, 2(4), 2369–2403. https://doi.org/10.3390/ma2042369

[43]. "Carbon Fiber – Toray." https://www.cf-composites.toray/products/carbon_fiber/index.html

[44]. Dassios, K. G. (2007) 'A Review of the Pull-Out Mechanism in the Fracture of Brittle-Matrix Fibre-Reinforced Composites', Advanced Composites Letters. https://doi.org/10.1177/096369350701600102

[45]. Sarasini, F.; Tirillò, J.; Ferrante, L.; Sergi, C.; Russo, P.; Simeoli, G.; Cimino, F.; Ricciardi, M.R.; Antonucci, V. Quasi-Static and Low-Velocity Impact Behavior of Intraply Hybrid Flax/Basalt Composites. Fibers 2019, 7, 26. https://doi.org/10.3390/fib7030026

[46]. Ozkan, Dervis & Gok, Mustafa & Karaoglanli, Abdullah. (2020). Carbon Fiber Reinforced Polymer (CFRP) Composite Materials, Their Characteristic Properties, Industrial Application Areas and Their Machinability. https://doi.org/10.1007/978-3-030-39062-4_20

[47]. Weihao Liu, Haihong Huang, Libin Zhu, Zhifeng Liu, Integrating carbon fiber reclamation and additive manufacturing for recycling CFRP waste, Composites Part B: Engineering, Volume 215, 2021,108808, ISSN 1359-8368, https://doi.org/10.1016/j.compositesb.2021.108808

[48]. Qi Zhao, Jianjun Jiang, Chuanbing Li, Yujun Li, Efficient recycling of carbon fibers from amine-cured CFRP composites under facile condition, Polymer Degradation and Stability, Volume 179, 2020, 109268, ISSN 0141-3910, https://doi.org/10.1016/j.polymdegradstab.2020.109268

[49]. S.A. Hadigheh, Y. Wei, S. Kashi, Optimisation of CFRP composite recycling process based on energy consumption, kinetic behaviour and thermal degradation mechanism of recycled carbon fibre, Journal of Cleaner Production, Volume 292, 2021, 125994, ISSN 0959-6526, https://doi.org/10.1016/j.jclepro.2021.125994

[50]. Soraia Pimenta, Silvestre T. Pinho, Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook, Waste Management,

Volume 31, Issue 2, 2011, Pages 378-392, ISSN 0956-053X, https://doi.org/10.1016/j.wasman.2010.09.019

[51]. "Waste Framework Directive – European Commission." https://environment.ec.europa.eu/topics/waste-and-recycling/waste-framework-directive_en

[52]. Esfandiar Pakdel, Sima Kashi, Russell Varley, Xungai Wang, Recent progress in recycling carbon fibre reinforced composites and dry carbon fibre wastes, Resources, Conservation and Recycling, Volume 166, 2021, 105340, ISSN 0921-3449, https://doi.org/10.1016/j.resconrec.2020.105340

[53]. Christelle Morin, Anne Loppinet-Serani, François Cansell, Cyril Aymonier, Near- and supercritical solvolysis of carbon fibre reinforced polymers (CFRPs) for recycling carbon fibers as a valuable resource: State of the art, The Journal of Supercritical Fluids, Volume 66, 2012, Pages 232-240, ISSN 0896-8446, https://doi.org/10.1016/j.supflu.2012.02.001

[54]. Takuma Hanaoka, Hiroki Ikematsu, Suguru Takahashi, Natsuki Ito, Noriaki Ijuin, Hiroyuki Kawada, Yoshihiko Arao, Masatoshi Kubouchi, Recovery of carbon fiber from prepreg using nitric acid and evaluation of recycled CFRP, Composites Part B: Engineering, Volume 231, 2022, 109560, ISSN 1359-8368, https://doi.org/10.1016/j.compositesb.2021.109560

[55]. Hongfang Sun, Guanping Guo, Shazim Ali Memon, Weiting Xu, Qiwu Zhang, Ji-Hua Zhu, Feng Xing, Recycling of carbon fibers from carbon fiber reinforced polymer using electrochemical method, Composites Part A: Applied Science and Manufacturing, Volume 78, 2015, Pages 10-17, ISSN 1359-835X, https://doi.org/10.1016/j.compositesa.2015.07.015

[56]. Chun Pei, Pi-yu Chen, Si-Cheng Kong, Junlin Wu, Ji-Hua Zhu, Feng Xing, Recyclable separation and recovery of carbon fibers from CFRP composites: Optimization and mechanism, Separation and Purification Technology, Volume 278, 2021, 119591, ISSN 1383-5866, https://doi.org/10.1016/j.seppur.2021.119591

[57]. Swaroop Gharde, Balasubramanian Kandasubramanian, Mechanothermal and chemical recycling methodologies for the Fibre Reinforced Plastic (FRP), Environmental Technology & Innovation, Volume 14, 2019, 100311, ISSN 2352-1864, https://doi.org/10.1016/j.eti.2019.01.005

[58]. Phuong Anh Vo Dong, Catherine Azzaro-Pantel, Anne-Laure Cadene, Economic and environmental assessment of recovery and disposal pathways for CFRP waste management, Resources, Conservation and Recycling, Volume 133, 2018, Pages 63-75, ISSN 0921-3449, https://doi.org/10.1016/j.resconrec.2018.01.024

[59]. R. Palmer, Identification and Comparison, Editor(s): Jay A. Siegel, Pekka J. Saukko, Max M. Houck, Encyclopedia of Forensic Sciences (Second Edition), Academic Press, 2013, Pages 129-137, ISBN 9780123821669, https://doi.org/10.1016/B978-0-12-382165-2.00092-1

[60]. Lirong Guo, Lei Xu, Yiyao Ren, Zhigang Shen, Rongzheng Fu, Han Xiao, Junyan Liu, Research on a two-step pyrolysis-oxidation process of carbon fiber-reinforced epoxy resin-based composites and analysis of product properties, Journal of Environmental Chemical Engineering, Volume 10, Issue 3, 2022, 107510, ISSN 2213-3437, https://doi.org/10.1016/j.jece.2022.107510

[61]. F. Meng, J. McKechnie, T.A. Turner, S.J. Pickering, Energy and environmental assessment and reuse of fluidised bed recycled carbon fibres,Composites Part A: Applied Science and Manufacturing, Volume 100, 2017, Pages 206-214, ISSN 1359-835X, https://doi.org/10.1016/j.compositesa.2017.05.008

[62]. Britannica, The Editors of Encyclopaedia. "solvolysis". Encyclopedia Britannica, 3 Oct. 2019, https://www.britannica.com/science/solvolysis. (accessed Jul. 2, 2022).

[63]. "Solvolysis – Wikipedia." https://en.wikipedia.org/wiki/Solvolysis (accessed Jul. 2, 2022).

[64]. "Supercritical fluid – Wikipedia." https://en.wikipedia.org/wiki/Supercritical_fluid (accessed Jul. 2, 2022).

[65]. "Critical point (thermodynamic) – Wikipedia." https://en.wikipedia.org/wiki/Critical_point_(thermodynamics) (accessed Jul. 2, 2022).

[66]. Raul Piñero-Hernanz, Christopher Dodds, Jason Hyde, Juan García-Serna, Martyn Poliakoff, Edward Lester, María José Cocero, Sam Kingman, Stephen Pickering, Kok Hoong Wong, Chemical recycling of carbon fibre reinforced composites in nearcritical and supercritical water, Composites Part A: Applied Science and Manufacturing, Volume 39, Issue 3, 2008, Pages 454-461, ISSN 1359- 35X, https://doi.org/10.1016/j.compositesa.2008.01.001

[67]. Yan Liu, Jie Liu, Zhiwei Jiang, Tao Tang, Chemical recycling of carbon fibre reinforced epoxy esin composites in subcritical water: Synergistic effect of phenol and KOH on the decomposition efficiency, Polymer Degradation and Stability, Volume 97, Issue 3, 2012, Pages 214-220, ISSN 0141- 910, https://doi.org/10.1016/j.polymdegradstab.2011.12.028

[68]. "Understanding Global Warming Potentials – EPA." https://www.epa.gov/ghgemissions/understanding-global-warming-potentials

[69]. Das, S. Life cycle assessment of carbon fiber-reinforced polymer composites. Int J Life Cycle Assess 16, 268–282 (2011). https://doi.org/10.1007/s11367-011-0264-z

[70]. Robert A. Witik, Remy Teuscher, Véronique Michaud, Christian Ludwig, Jan-Anders E. Månson, Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling, Composites Part A: Applied Science and Manufacturing, Volume 49, 2013, Pages 89-99, ISSN 1359-835X, https://doi.org/10.1016/j.compositesa.2013.02.009

[71]. Yoichi Kodera, Tetsushi Yamamoto, Eiji Ishikawa, Energy- and economic-balance estimation of pyrolysis plant for fuel-gas production from plastic waste based on bench-scale plant operations, Fuel Communications, Volume 7, 2021, 100016,ISSN 2666-0520, https://doi.org/10.1016/j.jfueco.2021.100016

[72]. A. Lopez-Urionabarrenechea, N. Gastelu, E. Acha, B.M. Caballero, I. de Marco, Production of hydrogen-rich gases in the recycling process of residual carbon fiber reinforced polymers by pyrolysis, Waste Management, Volume 128, 2021, Pages 73-82, ISSN 0956-053X, https://doi.org/10.1016/j.wasman.2021.04.044

[73]. "Heat of combustion – Wikipedia." https://en.wikipedia.org/wiki/Heat_of_combustion (accessed Sep. 12, 2022).

[74]. IEA (2019), The Future of Hydrogen, IEA, Paris https://www.iea.org/reports/the-future-of-hydrogen.

[75]. Gastelu, N., Lopez-Urionabarrenechea, A., Acha, E. et al. Evaluation of HZSM-5 Zeolite as Cracking Catalyst for Upgrading the Vapours Generated in the Pyrolysis of an Epoxy-Carbon Fibre Waste Composite. Top Catal 62, 479–490 (2019). https://doi-org.ezproxy.biblio.polito.it/10.1007/s11244-019-01152-7

[76]. "NIST Chemistry WebBook– NIST." https://webbook.nist.gov/chemistry/

[77]. Pirone R. "Slides from the course Utilizzo sostenibile delle biomasse a fini energetici, MSc in Energy and nuclear engineering (PoliTo)". Torino. And related references

[78]. Tranchard, P.; Samyn, F.; Duquesne, S.; Estèbe, B.; Bourbigot, S. Modelling Behaviour of a Carbon Epoxy Composite Exposed to Fire: Part I—Characterisation of Thermophysical Properties. Materials 2017, 10, 494. https://doi.org/10.3390/ma10050494

[79]. João Vitor F. Duque, Márcio F. Martins, Gérald Debenest, Marcos Tadeu D'Azeredo Orlando, The influence of the recycling stress history on LDPE waste pyrolysis, Polymer Testing, Volume 86, 2020, 106460, ISSN 0142-9418, https://doi.org/10.1016/j.polymertesting.2020.106460

[80]. "RYMYC" https://www.rymyc.it/

[81]. "RECARBON" https://recarbon.it/

[82]. "Gen2Carbon" https://www.gen2carbon.com/

[83]. "MANIFICA" https://manifica.eu/