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**Valutazione degli impatti ambientali e dei costi di un
innovativo processo per il recupero di sfridi di materiale
composito preimpregnato**

**Life Cycle Assessment and cost analysis of a new prepreg
scraps recovery system**

Tesi sperimentale

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INTRODUCTION

The use of composite materials is constantly increasing due to the growing number of possible applications. Composites are among the materials with the best specific properties such as specific stiffness and strength. Carbon fiber reinforced polymers (CFRPs) have a wide range of applications such as aerospace, automotive, energy and sporting. Some estimates predicted the worldwide demand for CFRPs to be over 140,000 tons this year, with a commercial value of nearly \$50 billion.

The increase in the use of these products has made it necessary to search for sustainable systems for their recycling. In fact, the production of composite materials, in particular carbon fibers composites, requires high energy consumptions and it is associated with a significant impact on the environment. In addition, European regulations for waste disposal are expected to become increasingly stringent in the future, making solutions such as landfill disposal economically disadvantageous. For example, the European legislation that regulates the end of life of automotive products states that at least 85% of the product must be recycled at the end of its useful life. The Directive 2008/98/EC of the European Parliament defined the waste management hierarchy where, after the prevention of waste production and the reuse of products, recycling is the most desirable choice. Recycling waste avoids solutions with a higher impact (i.e. the landfill) and leads to significant savings due to the reduction of the use of virgin materials.

Currently, there are several methods for the recycling of cured thermosetting CFRP waste such as mechanical recycling, thermal recycling, and chemical recycling. Typically, the properties obtained from recycled materials are lower than those of virgin materials; carbon fibers are often recovered after a cutting process of the waste that reduces the length of the fibers and consequently lowers their mechanical properties. The thermosetting polymers which constitute the composite's matrix are currently recovered as fillers or products for the chemical industry. The available recycling processes, while environmentally desirable, may not be cost-effective and companies often prefer landfill disposal for their production waste rather than a recycling scenario. This study evaluates the impacts and costs of a new recycling process for uncured thermoset matrix composite materials. In particular, the recovery

process regards the scraps produced during cutting operations of prepreg rolls (off-cuts, trim waste, and end-roll waste). Usually, these waste materials account from 20 to 50%wt of the prepgs produced. Since the prepreg rolls production is a very expensive and energy-intensive, the recycling of prepreg scraps is not only an environmental but also an economic necessity.

The new recycling system has been developed within the CIRCE project. CIRCE is a project developed as a collaboration between 5 Italian companies co-financed by the European Union as part of the LIFE programme. The objective is to prepare the prepreg waste to reuse them as secondary materials for new production processes.

This thesis aims to evaluate the environmental impacts and costs associated with new production systems which use the recycled material and to compare them to production systems currently used by the involved companies. The methodologies of Life Cycle Assessment (LCA) and Life Cycle Cost (LCC), defined in iso 14040 and 14044, have been followed.

The first part of this script (chapters 1-5) contextualizes the study that was carried out. the first chapter introduces the concept of concurrent engineering (CE) and design for environment (DFE). The second chapter explains in detail one of the DFE tool: the Life Cycle Assessment (LCA) analysis. Also, some of the most widely used environmental impact indicators and an introduction to the SimaPro software are included. Chapter 3 and 4 describe the materials and production processes considered later in the analysis. Then, chapter 5 presents some of the end-of-life scenarios currently available for composite materials, while chapter 6 introduces the case study of the analysis through a description of the CIRCE project. Chapter 7 and chapter 8 present two impacts and costs analyses that compare process based on the new recycled material to other processes available in the involved companies. Chapter 9, with the conclusions, ends the script.

CHAPTER 1

CONCURRENT ENGINEERING

1.1 Concurrent engineering: introduction

The traditional approach to design focuses primarily on the functionality of the product, and it does not consider all the aspects related to process planning, production, and the subsequent phases of the product's life. The activities needed for the product development are performed in succession (sequential approach) and there is not a systematic integration between them. For this reason, errors and inefficiencies are discovered in advanced stages of product development and corrections to the project are needed. The adjustments are made through time-consuming iterative processes, which may lead to delays.

Nowadays, the market is constantly evolving, and companies must respond quickly to the market requests with complex products with short life cycles. For these needs, and to reduce costs and lead time, a new approach to design was created: concurrent engineering (CE). This term was coined in 1980 (Stjepandić et al., 2015) and represents a series of methods and tools which allows, already from the design phase, to take in account several aspects of the life cycle of the product, such as production processes, marketing, and maintenance, not focusing only on the product function. CE is based on the principles of concurrency and simultaneity; thanks to multidisciplinary teams, the available knowledge and technology are coordinated, and the individual activities are carried out in parallel. This simultaneous approach makes the design phase more complex and expensive due to the greater number of aspects to be considered. Moreover, difficulties of coordination between the members of the team could emerge, so team training is needed to achieve good teamwork.

However, by mean of CE, the total cost of a project is reduced; many problems related to the manufacturing process are anticipated in the design phase. In this way, the number of design changes is high in the early stages, when the cost and time to carry them out is limited; in contrast, the number of changes during the manufacturing phase, when they would be more expensive and complicated to make, is close to zero. The increment of the cost of the design is compensated by an overall reduction of the project cost, of the wastes, and of the time to market. The cost of a project is defined for the most part by decisions taken in the design

phase%). If those decisions are adequate, money saving is obtained in the following phases., like in the case of concurrent engineering.

In figure 1.1, it is shown how, in a simultaneous approach, the allocated costs reach values higher than 80% in the design phase, because the important decisions are made in this early phase and in the following stages few changes are needed. On the other hand, the costs are incurred mainly in the production phase.

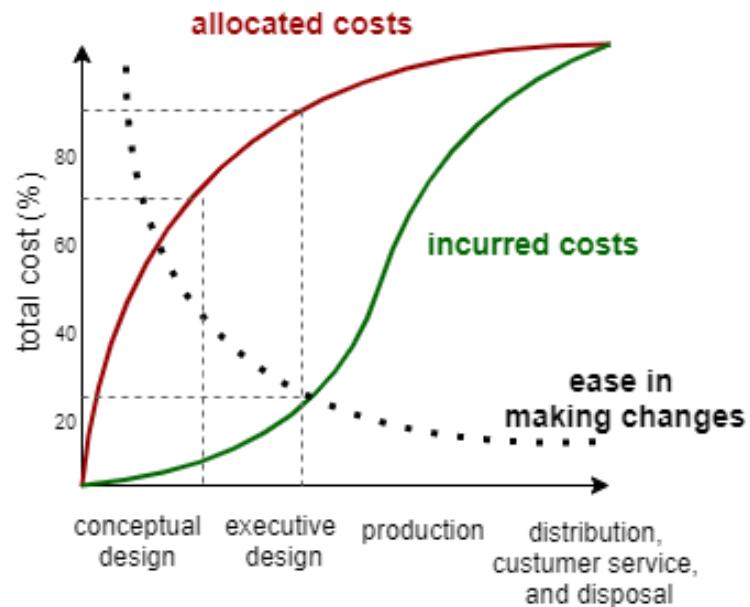


Figure 1. 1 allocated and incurred costs in a concurrent design approach

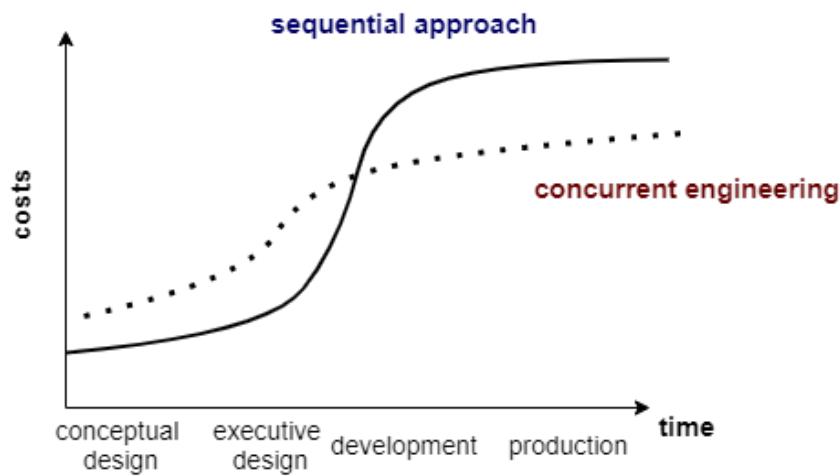


Figure 1. 2 concurrent engineering vs sequential approach costs timeline

Some of the benefits of CE are:

- Production development cycle time reduced by 40 to 60 percent
- Manufacturing costs reduced as much as 30 to 40 percent
- Scrap and rework reduced as much as 75 percent (Bertrand et al., 1988)
- it increases the flexibility
- the quality of the design is improved
- it raises productivity and efficiency
- it improves the social image of the company (Huang, 2018)

CE is not just a method or a tool, but it is a way of thinking that requires many methods and tools to be applied. It is a long-term business strategy which, if correctly implemented, provides benefits to the business. Implementing CE requires organizational and technical skills that are not easy to acquire. Gradual organizational development is needed to implement CE, moving from a sequential way of working to a parallel one. This is obtained by gradually increase the interaction and information exchange between people from different departments.

During the last decades, CE was subject of intensive research and development activities, and it evolved from the theoretical point of view and for the tool it uses. In 1994, ISPE (the International Society for Productivity Enhancement) introduced the annual international conference on Concurrent Engineering, which has the goal to share and discuss the most recent development of CE and its future objectives.

1.2 Design for x

Design for X (DFX) is one of the most effective approaches to implement CE. The X stands for the aspects that the design is intended to take into account. Among the types of DFX there are:

- Design for manufacturing (DFM)

DFM is a design methodology developed to make the manufacturing of the components of a product easy and economical. The designers give attention to all the possible manufacturing problems associated with a product. Since the middle of 1900, there have been works in the scientific literature dealing with these issues; such as “designing for production” by Niebel

and Baldwin (1957), and “Handbook of parts, forms, processes, materials in design engineering” by Everhart (1960).

- Design for Assembly (DFA)

DFA is the design of the product for ease of assembly. The goal of DFA is to make all the assembly operations as easy as possible. This approach has been studied since the middle of the last century and has undergone numerous evolutions. For example, in 1980 Hitachi developed the Assembly Evaluation Method (AEM), which was based on the principle of “one motion for one part”. In 1982 a DFA software was introduced for the Apple computer. (Boothroyd & Alting, 1992)

- Design for Manufacturing and Assembly (DFMA)

DFMA combines the two previous methodologies (DFM and DFA), and it considers all the issues related to manufacturing and assembly. It is a systematic procedure that reduces time and cost for product production. In order to reach the design goals, the working group follows several guidelines, such as:

- Reduction of the number of parts in a product
- Development of modular projects
- Use of standardized components
- Multifunctional parts design
- Multipurpose part design
- Design to make the manufacturing processes easy
- Selection of the most economical fixing method
- Reduction of assembly directions
- Reduction of handling operations

DFMA tools promote dialogue between designers and manufacturing engineers; team working is encouraged, and a concurrent engineering system can be achieved.

- Design for Environment (DFE)
- Design for Disassembly (DFD)

DFD involves developing products that are easy to take apart; in this way, the recycling and the removal of hazardous materials are facilitated. In the last years, research activity relied on DFD has increased dramatically; early investigations were conducted by BMW, starting from the middle of 1980s.

- Design for Recycling (DFR)
- Design for Remanufacturing (DFR)
- Design for Testability (DFT)
- Design for Electromagnetic Compatibility (DFEC)
- Design for Reliability and Maintainability (DFRM) (Gatenby & Foo, 1990)

1.3 Design for environment

Design for environment (DFE), also called Green Design or Environmentally Conscious Design, is a methodology developed to improve the environmental compatibility of a product. In the past, environmental issues were not considered during product development, but they were seen as specific problems affecting certain areas, such as waste disposal sites containing hazardous materials. Today, due to a better understanding and awareness of environmental problems, it is clear how the large part of the environmental impact of a product is dictated during the design and manufacturing phases. DFE considers the complete life cycle of a product, from “cradle to grave”, in order to minimise its effects on the natural systems. The design aims to meet human needs and to ensure services without compromising the availability of resources, limiting the environmental impact and the damages to human health.

In the last decades, the attention towards environmental issues has progressively increased, also considering their relationship with industrial and economic development. The World Commission on Environment and Development (WCED) ha defined, in the Brundtland report (1987), the concept of sustainable development, as a “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. This concept has had a great influence over industries works and how they relate to natural systems and has led to the creation of the “industrial ecology”(Giudice et al., 2006).

Several definitions of industrial ecology were formulated; however, they contain some common elements:

- Study of the flows of materials and energy
- Transformation processes considered cyclical (closed), rather than linear (open)
- A holistic vision of the interaction between industrial and ecological systems and harmonization between those two systems
- Creation of efficient and sustainable industrial systems

In this context, the design is a key factor in the development of sustainable production systems and products. Since the first half of the 1980s a new approach to design was developed, the DFE. Design for environment is a methodology directed at a systematic reduction or elimination of the environmental impacts related to the whole life cycle of a product. This design approach must be multidisciplinary, including technical, legal, economic, and political aspects. Technology has a major role in the search for solutions for environmental problems. The greatest benefits of DFE can be obtained taking into consideration the entire life cycle of a product during the design phase; in this way, the design team not only identifies the product's environmental criticalities but also reduces them effectively.

Throughout all the life cycle of a product, there are some guidelines which could help in reducing the overall impact on the environment:

- Materials selection
Recyclable and recycled materials are preferred. The presence of toxic substances must be minimised, as the quantity of materials used. Compatibility of different materials in the recycling phase must be considered.
- Production phase
Production processes must be optimized, considering the energy efficiency, the emissions, and the waste. Tools' production impact must be considered too.
- Transport phase
The packaging material quantity must be reduced and, when possible, packages must be reusable.
- Use phase

The design must increase products' energy efficiency and extend the products' useful life.

- Maintenance

The design must be concerned about creating a product which can be easily repaired and parts of it can be easily substituted in case of failures. In this way, the useful life of the part is increased.

- Demanufacturing phase

Strategies for the recovery of resources at the end of life must be planned, facilitating reuse, remanufacturing, and recycling, and reducing waste.

DFE aims to join the product development and environmental management, improving the environmental performance of products. This need comes from many factors from different fields. From the financial point of view, resource depletion and pollution are costly. It is not just a moral issue, but it is becoming a commercial imperative. The legislation is a relevant factor too; depending on the country, laws governing environmental problems may be more or less severe, but the common trend is a transition to more strict rules. The International Organization for Standardization, through its ISO 14000 series, has begun to standardize the implementation of environmental management systems and the tools that can be used. For example, the ISO 14062 is a technical report for the integration of environmental issues into product design and ISO 14040 and 14000 are about the LCA analysis (see chapter two). In the past, environmentally friendly products used to differ considerably from other products, in term of functional performance, appearance or cost. Nowadays, due to the new technologies, those problems can be overcome, and green products are spreading in the market.

DFE is implemented in design practice through three phases; in the first one, the target of the intervention (i.e. a product, a process, a resource flow...) is identified as well as possible alternatives (scoping). Then environmental data are acquired and evaluated. Lastly, the results of the first two phases are transformed into tools, such as simple guidelines or design procedures. This procedure is implemented using instruments to aid the analysis of the life cycle (life cycle assessment and life cycle cost) and the design or redesign (design for x methods).

CHAPTER 2

LIFE CYCLE ASSESSMENT ANALYSIS

2.1 Life cycle assessment: introduction

During the last century, the increasing interest in environmental issues has led to the development of techniques to assess the impacts on the natural system of human activities and industrial productions. Since the 1970s there have been studies to determine the effects of industrial activities on the environment, considering all phases of the product life cycle, from the initial gathering of raw materials to the disposal of waste (from cradle to grave). The traditional approach, which did not consider the entire systems of interrelated activities of the life cycle of a product, was inadequate and inefficient, in particular in relation to the environmental questions. In the 1970s, due to the oil crisis, the focus was directed to saving resources and to the study of the resources consumption; the study of the flows returning to the environment began to acquire a methodological structure.

SETAC (The Society for Environmental Toxicology and Chemistry), with a publication in January 1991, responded to the need for a standardized method to conduct these studies, defining the guidelines for the Life Cycle Assessment (LCA) (Vigon et al., 1993). The international standardization came in 1997, through the publication of the ISO 14040 series of norms that defined the LCA as a technique for assessing the impacts associated with a product by "*compiling an inventory of relevant inputs and outputs of a product system; evaluating the potential environmental impacts associated with those inputs and outputs; interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study*" (ISO 14040, 1997). LCA analyses all the interactions between the environment and the activities needed for the realization of a product in a holistic way. It considers several criteria that evaluate all the possible categories of environmental impacts and damages that may result from the processes. (14040, 2010)(ISO 14044 UNI EN, 2011)

The LCA has several possible advantages:

- It helps to improve the environmental performances of products during various stages of their life cycle, identifying critical issues and energy efficiency opportunities;

- It provides information to who, in governmental and non-governmental organizations, has to make decisions such as strategic planning, priority setting, product or process design or redesign;
- It supports the selection of environmental performance indicators and measurement technique; and
- It can add perceived value to products through marketing strategies that show the eco-sustainability of the company.

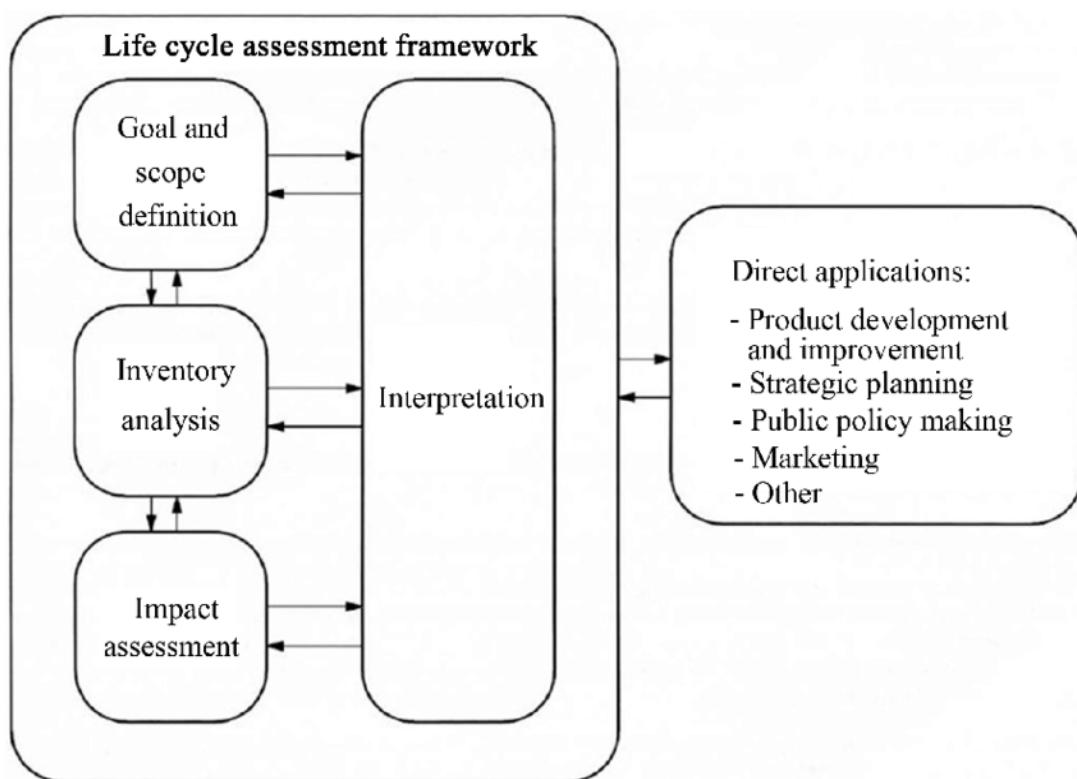


Figure 2. 1 life cycle assessment framework

2.2 LCA methodology

The LCA analysis is composed of four main stages:

1. Goal and scope definition
2. Inventory analysis phase or Life Cycle Inventory (LCI)
3. Impact assessment phase or Life Cycle Impact Assessment (LCIA)
4. Interpretation of the results

LCA is an iterative technique so, as data and new information are acquired, various aspects of the analysis can be changed.

2.2.1 Goal and scope definition

When defining the objectives of an LCA analysis, it is necessary to clearly describe the intended application and the reason for carrying out the study, such as the assessment of CO₂ emissions of a product or the creation of guidelines for improving the environmental performances of a process. The audience to whom the analysis is intended to be communicated should be identified. Moreover, this phase states whether the results are intended to be used in comparative evaluations to be disclosed to the public.

The scope includes the definition of the product system (or systems in case of comparative studies) which has to be studied. Other than that, other items are included:

- Functional unit

The functional unit is a quantified description of the performance requirements that the product system fulfils. It provides a reference to which the inputs and outputs are related, and it is fundamental for comparative analysis (in comparative studies the functional unit has to be the same for all the different systems considered). The functional unit, which can be, for example, a product, a process, a unit of material or energy, and a service, must be clearly defined and measurable to evaluate and compare the impact of all the scenarios.

- System boundary

The life cycle of a product is a series of consecutive stages, which perform one or more defined functions, connected by flows of materials and energy. The main phases are raw material acquisition, processing and manufacturing, distribution, use, maintenance, repair, recycle and, waste management. The system boundary determines which processes must be

included in the analysis. LCA can consider all those life cycle phases, evaluating all the activities “from cradle to grave”. However, a partial LCA can be conducted, defining one or more levels (gates) at which the complete system is interrupted. For example, the study might consider only the production processes of a factory (“from gate to gate”), or the useful life of a product (“from gate to grave”). The choice of not including phases of the product life cycle must be justified considering criteria in line with the study goal. Using flow charts can be useful to describe the material and energy flows of each life cycle phase.

- Data quality requirements

The quality requirements of the data used must be defined as it is linked to the reliability and accuracy of the results of the analysis. Typically, the following requirements must be met: time coverage, geographical coverage (data must be relative to the area considered for the study, i.e. the energy mix of a country), technological coverage, accuracy (data variability must be defined), completeness, representativeness, and consistency. Data sources must be specified, and any assumption must be justified. Flows and processes can be eliminated from the analysis considering the exclusion criteria, which are based on mass, energy, and environmental relevance. In order to avoid the omission of important inputs, the exclusion criteria must be clearly described.

During the scope definition phase are also defined.

- the allocation procedures
- the assumptions
- the limitations
- the type of critical review
- the type and format of the report required for the study
- the impact categories selected

2.2.2 Life cycle inventory

Life Cycle Inventory (LCI) consists in the compilation and quantification of the inputs and outputs of all the activities within the system boundaries. LCI involves both the quantitative and qualitative description of inputs and outputs. Like others LCA phases, LCI is an iterative procedure; as the data are collected and more information about the system are acquired,

new data requirements or limitations may be identified, so a change in the data acquisition procedures may be necessary. Sometimes, even the goal and scope of the study need to be changed.

The inputs include the energy, the raw materials, and other ancillary inputs. The output side includes all the product, co-product, and waste, and all the emissions to air and discharges to water and soil. Using those inputs and outputs, a flow model of the system is created. The flow chart helps to clearly describe the system boundaries. The inventory data can be collected from multiple sources, like scientific literature, scientific books, market information, environment database, direct measurements, and questionnaires with process operators. Data quality is a crucial aspect of this phase; if some information does not respect the quality requirements, it should be declared in the study report.

After the data have been collected, the following steps are carried out:

- Validation of data collected
 - To assure that the data quality meets the requirements of the study. Since all the unit processes obey the laws of conservation of energy and mass, mass and energy balances may be useful to control the processes.
- The relating of data to unit processes
 - Using the flow chart, all the inputs and outputs must be related to the functional unit
- The relating of data to the reference flow of the functional unit.

Most industrial processes yield to multiple products and they use intermediate or discarded products as raw materials. This leads to the need of allocation procedures, which have to be documented and clearly defined. Allocation procedures must be applied uniformly to all the inputs and outputs of the system; whenever is possible, allocation procedures must be avoided.

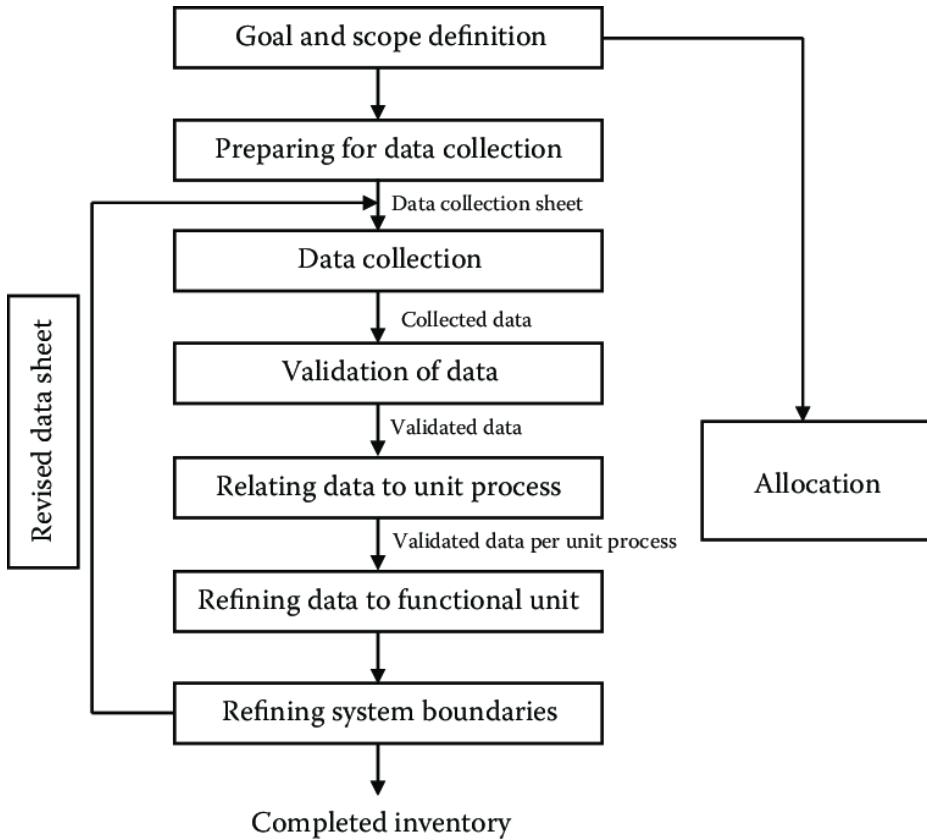


Figure 2. 2 LCI phases

2.2.3 Life cycle impact assessment (LCIA)

The Life Cycle Impact Assessment is the phase of LCA where the data gathered in the LCI phase are translated into potential environmental impacts.

The LCIA is composed of three obligatory stages:

1. Selection

Consist in the choice of the impact categories and impact indicators to consider in the LCIA (some example impact categories are explained in section 2.3); the environmental effects to be taken into consideration are chosen depending on the scope of the study.

2. Classification

The inventory data are associated with the various impact categories

3. Characterization

The characterization aims to quantify the value of the environmental indicators. The impact of every consumption or emission is calculated by multiplying the quantity consumed or emitted, by the respective impact assessment factor (or characterization factor) relative to each impact category. The accuracy of the results depends on the accuracy of the previous phases of the analysis

And three additional stages:

1. Normalization

The environmental impact scores of an LCIA are often difficult to interpret because of the units of measurement used for the impact indicators (i.e. kg CO₂ eq). Normalization allows an easier understanding of the results. It consists in dividing the scores by reference scores, like for example the annual emission and resource use of an average person. In this way, the results are converted into fractions of the reference scores.

2. Grouping

Grouping consists in sorting and ranking the impact categories used.

3. Weighting

The different impact categories are weighted in relation to each other. All the results can be aggregated to a single score for the total environmental impact.

Further analysis can be made, such as:

- Gravity analysis

It identifies the elements with a higher impact on the scores results.

- Uncertainty analysis

It investigates how the data uncertainties influence the results.

- Sensitivity analysis

It determines how the method and the data choice influence the LCIA results.

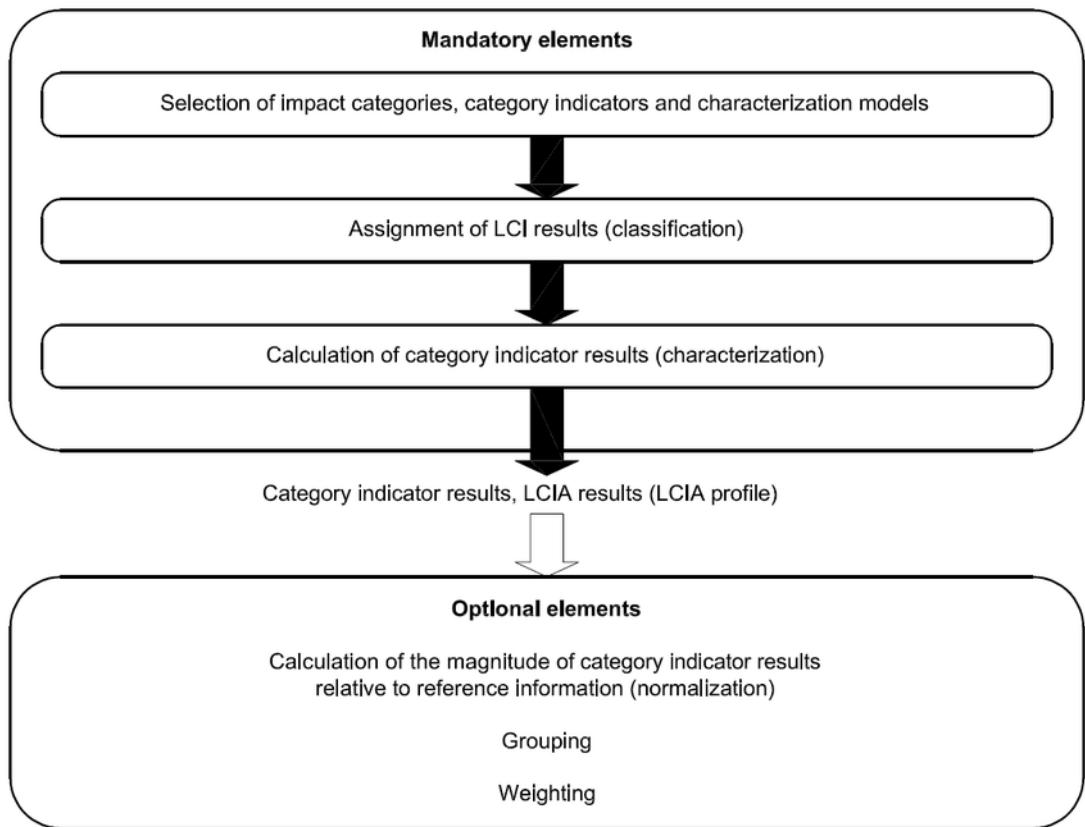


Figure 2. 3 obligatory and optional elements of the LCIA

2.2.4 Life cycle interpretation

In the last phase of the analysis, the results of the LCI and the LCIA are correlated and interpreted considering the objective and the application of the study.

The most significant factors for the environmental impact are identified. They can be, for example, inventory data (such as emission, energy, or waste), impact categories (climate change, resource depletion etc.) or processes and group of processes (i.e. the all the transports or the energy production). The study is then evaluated, considering completeness, sensitivity, and consistency checks. The first control is used to check if the data are all available and complete; the second one to evaluate how the results are influenced by data uncertainties, allocation methods and others factors; the last control is needed to check if the hypothesis, the methods used and the data are consistent with the scope and application of the analysis. Lastly, conclusion, limitations and recommendation are made, in order to reduce the environmental impact of the process studied.

2.2.5 LCA applications area

LCA has several possible applications in the field of environmental management. It helps to include environmental aspects into product design, development, and production standards. It is a useful tool for the quantification, the monitoring, and the reporting of the project emissions and the verification and certification of greenhouse gas emission. It allows obtaining environmental labels (eco-labelling) that certify that a product or a process is environmentally preferable considering certain impact categories.

Moreover, there are other techniques, methods and tools that use the same life cycle approach of LCA and have other advantages; some examples are environmental impact assessment (EIA), environmental management accounting (EMA), hazard and risk assessment of chemicals, life cycle management (LCM) and life cycle costing (LCC).

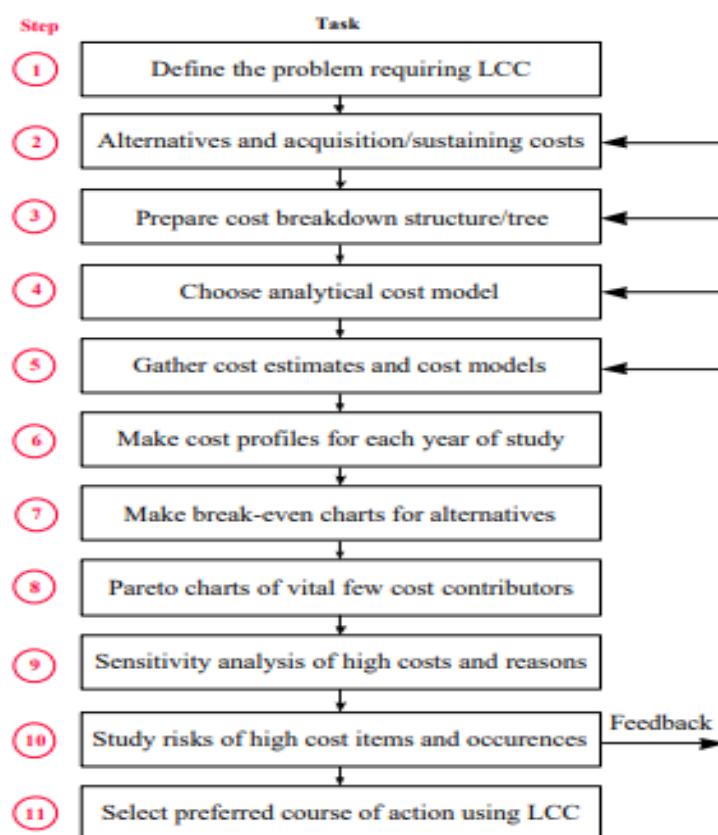


Figure 2. 4 Life Cycle Costing phases

Life cycle costing is a method, first developed in the min 1960s, used to estimates all the cost related to a product by mean of an analytical study. The main goal of this study is to choose

the most economically convenient approach among a series of possible alternatives. It can consider all the costs of the design, development, production, maintenance, support, and final disposal in a life cycle approach. LCC requires a high volume of data and often only a few are available, so the outputs are only estimated; however, this technique has proven its usefulness during the years. The main steps of the LCC are resumed in figure 2.4

2.3 Impact categories

The goal of every LCIA is to achieve relevant, clear, and easy to manage and communicate results. For this reason, the choice of impact categories and indicators is crucial. This choice depends on the specific case and is not always obvious; different methods can lead to important differences in the results. Using different methods within the same study can give a complete vision of the impacts of a product. The software SimaPro offers a wide choice of methods to use and some of them are described as follow.

2.3.1 CML

CML is one of the first methods made available and it was developed by the Center of Environmental Science of the Leiden University, Netherlands (Centrum voor Milieukunde Leiden: CML). The methodology was published In English in the summer of 1993 (Heijungs et al. 1992: Guide and Backgrounds). The main impact categories considered by the CML method are referred to resources and energy consumption, and pollution (i.e. climate change, ecotoxicity, ozone layer depletion, acidification, and eutrophication)

2.3.2 The Eco-Indicator 99

The Eco-Indicator 99 (Goedkoop & Spriensma, 2001) derived from the updating and improvement of the Eco-Indicator 95 method. The project was commissioned as part of the Integrated Product Policy, in the Netherlands, by the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM), with the aim of developing a new methodology to be used for products development application. It considers three types of environmental damages (endpoints):

1. Human health, expressed in DALY (Disability Adjusted loss of Life Years)
2. Damages to Ecosystem Quality expressed as a percentage of all species that have disappeared in a certain area due to the environmental load

- Resource extraction expressed in MJ surplus energy; it considers that the extraction of resources will result in higher energy requirements for future extraction.

2.3.3 Cumulative Energy Demand

The Cumulative Energy Demand (CED) or primary energy consumption quantifies, by mean of characterization factors, all the direct and indirect energy used by a product. It includes the consumption of all the processes included in the system boundaries, such as the extraction of raw materials, the production, and the disposal phase. CED is expressed in MJ and it is the sum of the demand of fossil, nuclear, wind, hydroelectric and solar energy utilized during the life cycle phases taken in account for the study. Since the first LCA analysis, the primary energy consumption has been one of the key indicators used and even today is often employed. Despite that, there is still no standardization and unification for this method and several approaches are today available (i.e. the energy harvested approach) (Frischknecht et al., 2015).

2.2.4 IPCC Greenhouse Gas Emission

The Global Warming Potential (GWP) is used to quantify greenhouse gases (GHG) emissions into the atmosphere and their effect on global warming and climate change. It considers the heat absorbed by any greenhouse gas as a multiple of the heat that would be absorbed by the same mass of carbon dioxide (CO_2) and assess their effects over the years. Estimates of GWP values over 20 and 100 years are periodically compiled in reports by the International Panel on Climate Change (IPCC). (Physical & Basis, 2013)

In the table below (2.1) are reported some values of GWP taken from the fifth assessment report (AR5) of the IPCC.

	Lifetime (yr)	GWP	
		Cumulative forcing over 20 years	Cumulative forcing over 100 years
CO_2	b	1	1
CH_4	12.4	84	28
N_2O	121.0	264	265
CF_4	50,000.0	4880	6630
HFC-152a	1.5	506	138

Table 2. 1 example values of GWP taken from the fifth assessment report (AR5) of the IPCC

2.2.5 ReCiPe

ReCiPe is a method for the LCIA phase first developed in 2008 that provides a “recipe” to calculate life cycle impact category indicators. The acronym represents the initial of the institutes that contributed to the project: RIVM and Radbound University, CML and PRè. This method unites two different approaches and gives results at both the midpoint (like CML) and endpoint (like Eco-indicator 99) levels.

Eighteen impact categories are addressed at the midpoint level. They focus on specific environmental problems and their evaluation provides a comprehensive view of the effect of a product or a process on the environment. They are listed as follow:

1. climate change (CC)
2. ozone depletion (OD)
3. terrestrial acidification (TA)
4. freshwater eutrophication (FE)
5. marine eutrophication (ME)
6. human toxicity (HT)
7. photochemical oxidant formation (POF)
8. particulate matter formation (PMF)
9. terrestrial ecotoxicity (TET)
10. freshwater ecotoxicity (FET)
11. marine ecotoxicity (MET)
12. ionising radiation (IR)
13. agricultural land occupation (ALO)
14. urban land occupation (ULO)
15. natural land transformation (NLT)
16. water depletion (WD)
17. mineral resource depletion (MRD)
18. fossil fuel depletion (FD)

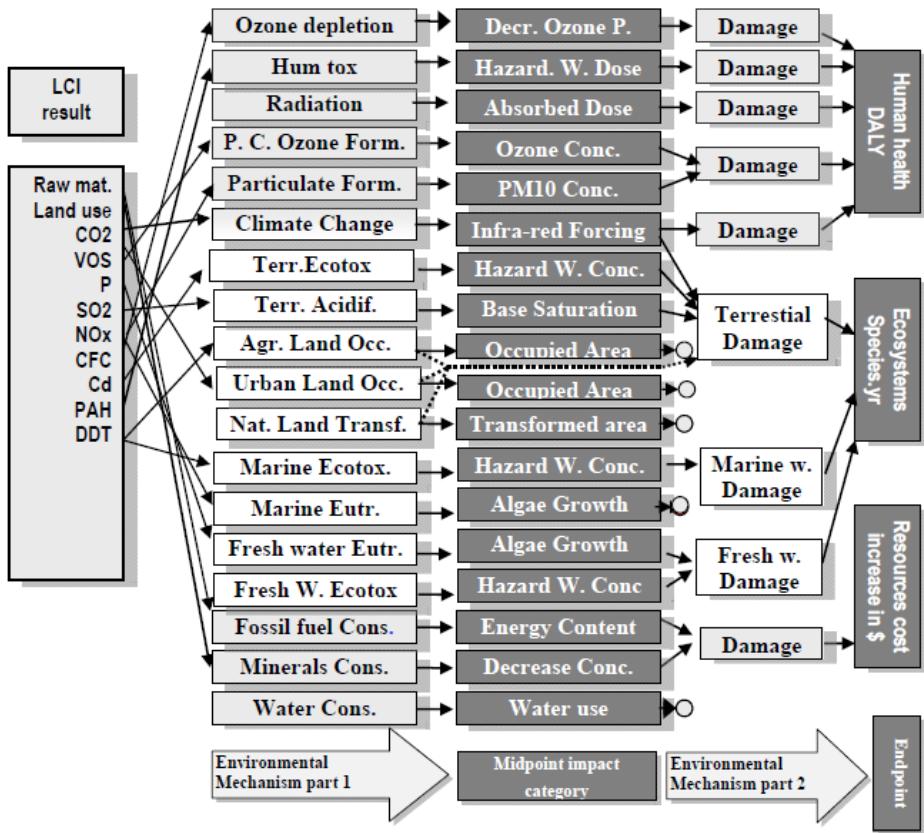


Figure 2.5 ReCiPe impact categories

Most of these midpoint impact categories are then aggregated into three endpoint categories:

1. damage to human health (HH)
2. damage to ecosystem diversity (ED)
3. damage to resource availability (RA)

Aggregating the midpoint categories makes the results easier to interpret but increases the uncertainty of the results.

Figure 2.5 shows all the impact categories and the links between the midpoint and endpoint levels. Note how some midpoint categories are not considered for the calculation of the endpoint results. The ReCiPe method was developed over European-scale models to be as general as possible. In fact, some environmental mechanisms (i.e. acidification, eutrophication, toxicity etc.) depend on the regional condition. For this reason, the ReCiPe

method has limited validity for all regions that cannot be defined as well-developed temperate regions. (

2.4 SimaPro

The SimaPro software is produced by the Dutch company Prè Consultant and, nowadays, it is one of the most used software to conduct LCA studies. It is used in over 80 countries by industries and academics to evaluate the environmental performances of various products, processes, and services. It is used for several applications such as carbon and water footprinting, product design, generating environmental product declarations and determining key performance indicators (<https://simapro.com/>).



The main features of SimaPro are:

- The possibility of choosing between different packages, depending on the user needs.
- Intuitive user interface following ISO 14040.
- Easy modelling, with the “Wizard” section for user assistance.
- Parametrized modelling with scenario analysis. This allows, for example, to perform sensitivity analysis, analysis of uncertainty, and to define non-linear relationships between the different parameters.
- Direct linking to Excel or ASP database.
- Direct impact assessment calculations from each stage of the model.
- Monte Carlo analysis.
- Results available in graphs and tables.
- Interactive analysis of the results, with the possibility of trace results back to their origins.

- Grouping of results.
- Weak point analysis. The process tree can be used to identify any “hot spots”.
- Single or multi user.

The SimaPro software includes many inventory databases that include thousands of processes and materials. Some examples of databases are reported as follows:

- Ecoinvent 3

It is included by default in the software and it is the largest ad most consistent LCI database in the market. It includes more than 15'000 LCI datasets in the areas of energy supply, agriculture, transport, biofuels and biomaterials, bulk, chemicals, construction materials, textiles, basic and precious metals, metal processing, electronics, dairy, wood, and waste treatment



- Agri-footprint

Agri-footprint is a database completely focused on agricultural products. It provides information about bio-based production methods for the chemical and energy industry. It contains approximately 5'000 products and processes specific to agricultural LCA



- US Life Cycle Inventory database

The U.S. Life Cycle Inventory database (USLCI) allows to consider energy and materials flows associated with production systems In the U.S.

- ELCD

ELCD (European Life Cycle Database), developed by the European Platform on Life Cycle Assessment (EPLCA), is a database that contains more than 500 datasets with

data on industry production (i.e. for the chemical and metal industry), energy production, transport and end-of-life processes.

- Industrial data 2.0

It contains data collected by industrial associations. Currently, it contains processes from PlasticEurope, Wordsteeel and ERASM (European Detergents and Surfactants Industries)

- Swiss Input/Output database
- LCA Food DK
- EU and Danish Input Output

CHAPTER 3

COMPOSITE MATERIALS

3.1 Introduction to composite materials

Composite materials (or composites) are materials made from two or more constituent with different physical and chemical properties. They are usually made of a high strength discontinuous phase (the reinforcement) embedded in a continuous phase (the matrix) with a distinct interface between them. The two elements retain their physical and chemical identities, but the resulting properties exceed the constituents acting alone. In general, the load is mainly carried by the reinforcement, which has high mechanical properties, while the matrix transfers the load to the reinforcement, keeps it in the desired position and orientation, and protects it from environmental damages.

The market of composites is continuously grooving (Vita et al., 2019) as those materials have remarkable properties such as flexibility, high corrosion resistance, lightweight, impact strength, and fatigue strength. They are being considered as a replacement for traditional materials in different applications, such as automotive and aerospace. The engineering properties required by the product can usually be achieved with a selection of the reinforcement and the matrix, done considering different aspects like type of loading (axial, bending, torsion...), mode of loading (static, fatigue, impact...), service life, operating environment, cost, and manufacturing processes available.

Composites can be classified at two different levels: considering the matrix material and the reinforcement geometry. The main composites' families encompass metallic matrix composites (MMC), ceramic matrix composites (CMC), and polymer matrix composites (PMC, either with thermoplastic or thermosetting matrix). About the reinforcement phase, it can be of two kinds: in continuous lengths (long fibers) or discontinuous length (short fibers, particles, and whiskers). In general, composites' properties strongly depend on the directions in which the fibers are placed, so usually composites are not isotropic materials, like traditional metals.

In the past, the production of these materials was developed only for the aerospace industry, where costs and production volume are not as important as parts' quality. In the last decades, several manufacturing techniques were developed and the cost of composites per volume unit reduced, becoming competitive to traditional materials. Nowadays, composite materials are used in a wide number of lightweight applications like body, chassis and engine components for the automotive sector, sports equipment (tennis racket, athletic shoes...), marine applications or civil infrastructures, replacing concrete and steel.

In the following paragraphs, the focus is directed towards PMC, carbon fibers, epoxy and phenolic resin as those materials are considered in the present study.

3.2 Polymer matrix composites

Polymer matrix composites constitute a major category of composite materials and they offer a combination of strength and modulus that can be even better than many traditional metallic materials. As the other composite's categories, they are constituted of two components, the matrix, and the reinforcement. The matrix can be made of a thermoplastic or a thermosetting polymer.

Thermosets are the most commonly used polymers, and they are hardened by curing, a bonding chemical process based on cross-linking of polymer chains. The starting material for curing is a powdered or liquid prepolymer and the polymerisation process starts due to the application of heat or the effects of chemical agents. The chemical bonds created during the curing process are irreversible, so if reheated, thermosets will not melt but they will turn from a hard to a viscous or rubbery state at the glass transition temperature (T_g), that depends on the resin type. Keep heating the polymer over the T_g may even cause its degradation, so thermosets are not recyclable. There are two main transformations during curing: gelation and vitrification. The process starts with uncured material (A-stage) and with heat or crosslinking agents the polymerization begins so bonds between polymer chains are created. Gel point is defined as the moment at which covalent bonds connect across the network and produce a material of infinite molecular weight (B-stage)(Cadenato et al., 1997). The material's viscosity increases, creating an elastic gel that can still be molded but cannot flow as easily as a liquid resin; for this reason, at this stage, the resin must have already flowed into

the mold and wet out the reinforcement fibers. The vitrification point is the time at which the materials solidify and crosslinking stops (completely cured material, C-stage). At this point, the glass transition temperature equals the curing temperature, due to the phase transformation, from rubbery to the glass material.

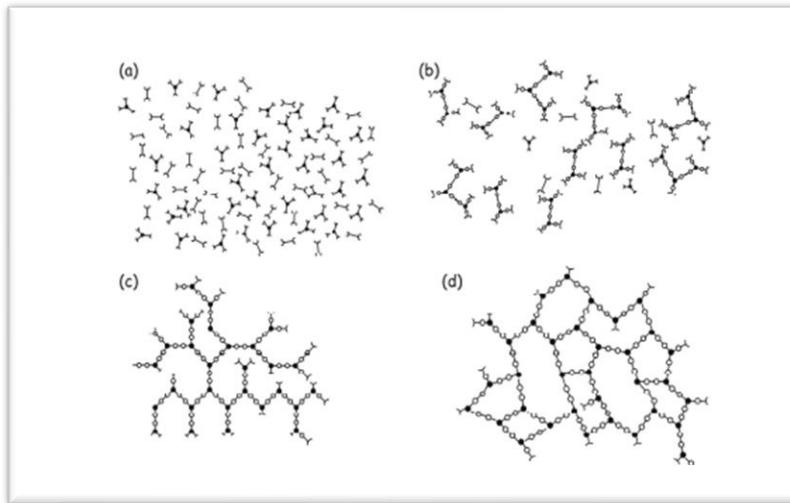


Figure 3. 1 Curing stages. a) raw material b) polymerization begins, bonds between monomers c) gelation d) vitrification

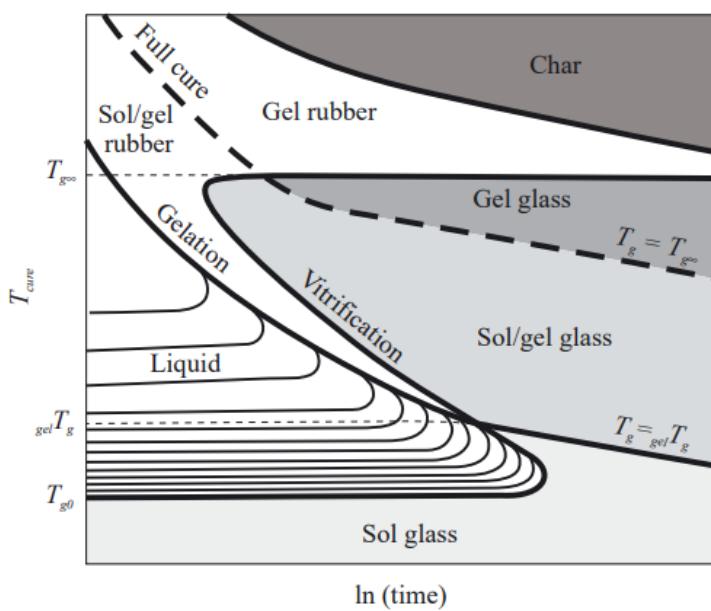


Figure 3. 2 time-temperature-transformation cure diagram

The resin behaviour during curing can be predicted using time-temperature-transformation (TTT) cure diagram, which shows the time required to reach various states of material during isothermal cure with a certain curing temperature (T_c). (Urbaniak & Grudziński, 2007). The diagram, as it can be seen in figure 3.2, shows the material states that resin can reach during curing and the time required for the gelation and the vitrification. Other than that, three characteristic temperature are shown: T_{g0} , below which no significant reaction occurs, $_{gel}T_g$, the temperature at which, in an ideal system, gelation and vitrification happen simultaneously and $T_{G\infty}$ that is the glass transition temperature of an ideal fully reacted material (with conversion degree $\alpha=1$). The most used resins for high-performance application are polyester, epoxy, phenolic, silicon, vinyl ester, and bismaleimides.

Thermoplastic polymers are materials that became moldable at a certain elevated temperature as their viscosity drastically decreases. The intermolecular forces (Van der Waals, hydrogen bonding...) between the polymer chains, weaken as the temperature increases and the material becomes a viscous liquid that can be easily shaped. This process can be repeated as the intermolecular forces are not irreversible like the chemical bonds of curing, and since no chemical reaction is required, the molding process is faster for thermoplastics. Even if in theory they are recyclable, after repeating the process several times, polymer degradation may occur, and the mechanical properties of the recycled part may be lower than the virgin product. Due to the high molecular weight of thermoplastics, viscosity is much higher than thermosets. The raw material is cheap, production processes are fast, they are recyclable, weldable and they have good impact resistance. Some of the most common thermoplastic resin are polyamides, polyether ether ketone (PEEK), polyethylene (PE), polyphenylene sulphide (PPS) and polypropylene (PP).

About the reinforcements, fibers, either short or long, are the most used. They have high specific strength and high specific modulus. The fibers' volume fraction can be controlled, and the fibers' configuration can be adjusted to guarantee optimum properties in a specific direction. Reinforcement fibers are either natural fibers (i.e. mineral and cellulose fibers) or synthetic fibers (glass, aramid, or carbon fibers). Various forms of long fibers are used such as monofilament, tow, yarn, roving, mat, tape, and fabric.

The performance of a fiber-reinforced polymer (FRP) composite strongly depends on the quality of the fiber-matrix interface, which determines the way by which loads are

transferred from the matrix to the reinforcement. During production processes, the resin flows and coats the reinforcement (wet-out) and bonds are created between fibers and resin. Those bonds can be of four different types: mechanical bonds, which increase if the fibers have a roughened surface, physical bonds, resulting of electrostatic intermolecular forces (i.e. Van Der Waals, ionic bonding, and hydrogen bonding), chemical bonds, and bonds created by applying adhesive promoter. Various methods are employed to improve the roughness and the activity of the fibers' surface like, for example, surface oxidation or the use of sizing agents. Sizing consists in the application of a thin layer of coating on the fibers. This process, other than improving adhesion between fibers and matrix, improves fibers' mechanical properties, chemical resistance, and thermal stability.

3.3 Carbon fibers

Carbon fibers (CFs) were produced for the first time in the second half of the 19th century and they were used by Thomas Edison in one of the first incandescent light bulbs.(Morgan, 2015). The carbon filament used by Edison had poor mechanical properties but during the 1950s, researchers focused on finding a new production method to create a much stronger grade of carbon fiber. CFs consist mainly of turbostratic carbon. Carbon atoms are bonded together in crystals that are aligned parallel to the long axis of the fiber; this structure gives the fiber high specific strength.(Khurshid, 2019)

Nowadays, CFs available in the market have a diameter of around 5-10 µm and a tensile modulus between 207 GPa and 1035 GPa. These fibers have several advantages such as high modulus and strength, thermal and electrical conductivity, creep resistance, thermal shock resistance, chemical inertness, and low thermal expansion. The main disadvantages are the low impact resistance, the low strain-to failure, and the high production costs. CFs are primarily used in high-technological applications (i.e. space and aeronautics) but their application widened even in civilian sectors such as automotive and sports equipment. At present, carbon fibers are manufactured by thermal decomposition of various organic fiber precursors. The popular precursors are polyacrylonitrile (PAN) polymers, pitch, and rayon.

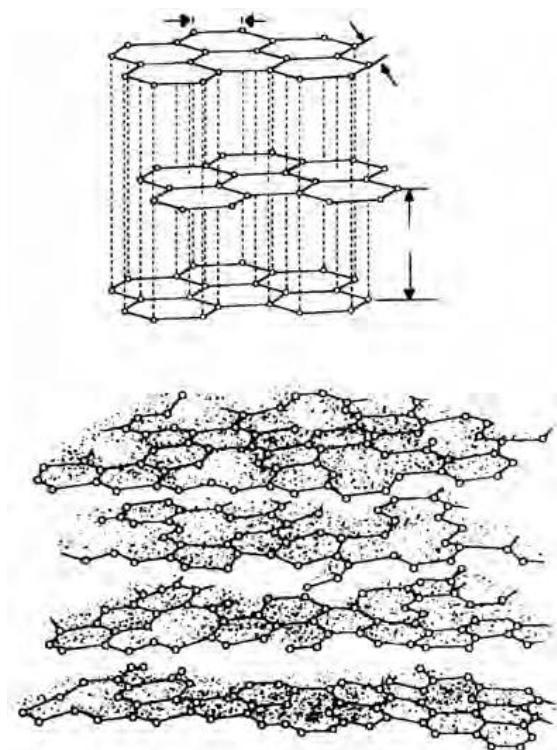


Figure 3. 3 crystal structure if graphite crystal (up) and structure of turbostatic carbon (down)

3.3.1 Polyacrylonitrile-based carbon fibers

PAN is an atactic linear polymer consisting of a carbon backbone with carbon-nitrogen (CN) pendent groups. The PAN precursor to produce carbon fibers needs to have high molecular weight, high strength, high modulus, minimum molecular defects, and high carbon yield. PAN fibers are obtained by polymerisation of acrylonitrile (AN), using dimethylformamide (DMF) as a solvent. AN, along with acrolein, is an output of the SHOIO process (Hanna, 2004), which is the selective oxidation and ammoniation of propylene. DMF is obtained by a catalysis reaction between dimethylamine and carbon monoxide (Duflou et al., 2009).

To produce CFs from PAN the following steps are considered:

- 1) Spinning and stretching of PAN precursor
- 2) Stabilization at 220 °C in air under tension
- 3) Carbonization
- 4) Graphitization

- Spinning and stretching

In the first phase, PAN plastic is prepared by using a polymerization process and then PAN fibers are created by spinning the plastic. The spinning can be performed by a thermal process or by a solution-based process; during this step, the atomic structure of the fibers is formed. A subsequent stretching of the spun fibers helps to reach the desired diameter and the molecular alignment of the polymeric chains.

- Stabilization

Before carbonization, the linear structure of the fibers must be converted into a more stable structure. This is done by heating them at 220 °C for 30-120 minutes. Fibers react with oxygen and rearrange their molecular structure in a ladder architecture; the process is exothermic, so careful controls are needed to avoid overheating of the fibers.

- Carbonization

Polyacrylonitrile fibers are heated up to a temperature between 900 °C and 1400 °C. The furnace has an inert atmosphere and a pressure higher than atmospheric pressure. In this way, thermal decomposition of the polymers takes place and water, and other volatile by-products (NH₃, CO, CO₂, N₂...) are produced. The remaining carbon atoms are crystallized to turbidostatic/graphitic layers aligned parallel to the fiber axis. During this phase, the mechanical properties of the fibers increase. Since the fibers' surface obtained in this way is inactive, further processes are needed to guarantee strong bonding with the polymers used in composites production. Functional groups containing oxygen can be developed on the surface of the fibers by an oxidation process, making the fibers react with various gases (air, CO₂...) or liquid (i.e. nitric acid). The surface oxidation provides even a roughened surface. After the surface treatment, the fibers are coated with sizing agents to protect them from damages during the following procedures (Professor A. Forcellese course notes).

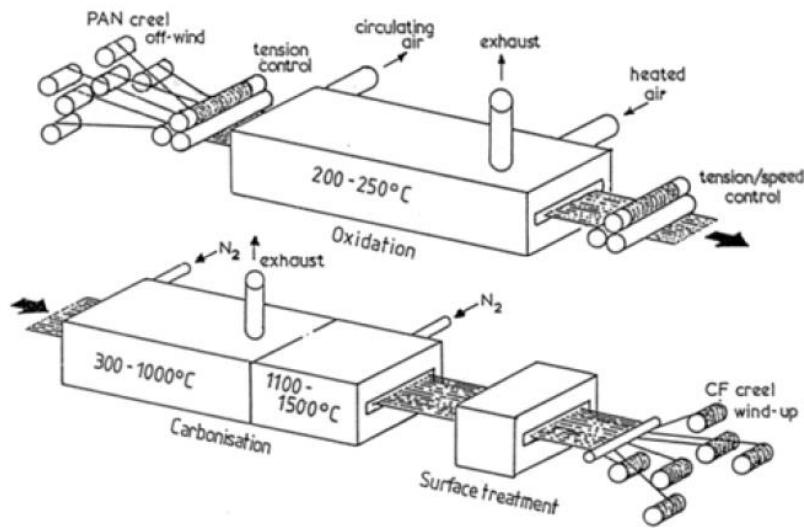


Figure 3. 4 carbon fibers production process.

- Graphitization

Graphitization consists in heating the carbonized fibers in an inert atmosphere to high temperature, typically between 1900 °C and 2500 °C. In this way, the crystalline order is improved and consequently, the tensile modulus of the fibers is improved. The tensile modulus of the fibers highly depends on the heat treatment; the higher the temperature, the higher the tensile modulus.

PAN-based carbon fibers can be classified considering their tensile modulus (E) and their tensile strength (σ_r) as follow:

- UHM (ultra-high modulus). $E > 500 \text{ GPa}$, $\sigma_r \simeq 3,5 \text{ GPa}$
- HM (high modulus). $350 \text{ GPa} < E < 500 \text{ GPa}$, $\sigma_r \simeq 2 \text{ GPa}$
- IM (intermediate modulus). $E \simeq 300 \text{ GPa}$, $\sigma_r \simeq 2 \text{ GPa}$
- LM (low modulus). $E < 100 \text{ GPa}$
- HTS (high tensile strength). $E \simeq 250 \text{ GPa}$, $\sigma_r > 4 \text{ GPa}$

3.4 Thermosetting resins

Two of the most commonly used thermosetting resin are described as follow.

3.4.1 Epoxy resin

Epoxy resins are a class of polymers firstly developed at the end of the 20th century and introduced in the USA market in the late 1940s. Nowadays epoxies are widely used in modern industries with a large number of applications. The term epoxy refers to the base uncured resin as well as the cured cross-linked thermoset plastic. Chemically those resins are defined by the presence of α -groups. The properties of epoxy resins can vary depending on the production processes and the formulation's ingredients, but some generalizations about their characteristics are possible. Liquid resin can be easily molded thanks to its low viscosity; curing temperature is between -40 °C and 200 °C, depending on the curing agents used. During cure, no volatile by-products are generated. Epoxies wet and adhere well to many surfaces; (Dodiuk & Goodman, 2013) for their high bonding strength, they are one of the major types of structural adhesive used in human life. They are electrical and thermal insulators, and they have good chemical resistance. The most common type of epoxy resin is the Diglycidyl Ether of Bisphenol A (DGEBA).

3.4.2 Phenolic resin

Phenolic-formaldehyde resin (phenolic resin, PF) is considered the first thermosetting plastic which became commercially available. In fact, studies about phenol and formaldehyde were conducted as early as 1872 by Adolf Bayer. The use of PFs was diffused after 1907, thanks to Dr H. Baekeland and his "heat and pressure" patent. He is known as the "father of phenolic resins" and one of the most popular resins on the market was named Bakelite after the company he formed in 1910. PFs are formed mainly by a polycondensation reaction between phenol (C_6H_5OH) and formaldehyde (CH_2O). Those kinds of resin are usually available in liquid form, but films, flakes, and powder forms are possible too. Powdered resin can be obtained starting with a blend of liquid prepolymer (novalac and resole resins) which then is spray dried.

There are several forms of phenolic resins and their properties depend on the use for which they are created. For example, there are casting, adhesives, bonding, coating, molding, and laminating resins. In 2004, wood adhesives occupied 69% of the phenolic resins market. Although molding resins constitute only about 6% of the market, a wide range of products

derives from those materials. Phenolic molding resins can be easily shaped with good dimensional stability and accuracy. They have good heat, electrical and chemical resistance. Moreover, they have high deformation resistance under load.

Phenolic-formaldehyde resin production is estimated to be around 3,5-4 million tons/year.

3.5 Prepreg

Prepreg is a pre-impregnated composite material where fibers are embedded in a polymer matrix. Different forms of reinforcements are used for the prepreg production, like nonwoven mat, woven fabric, and roving; different kinds of fibers (carbon fibers, glass fibers...), and resins (phenolic resins, epoxy resins...) can be used for the prepgs production. Prepgs offer several advantages such as better control of the resin and reinforcement content, impregnation uniformity and, high mechanical properties of the final product.

Laminates are created using several layers of either unidirectional continuous fiber prepgs or bi-directional fiber prepgs (Mallick, 2010). The stacking procedure allows complete control over the fibers' orientation, which can be varied from layer to layer. Using prepgs reduces the risk of poor impregnation quality because the correct amount of each constituent material is obtained during the production of prepgs. Typically, prepg consists of a single layer of fibers in a B-staged thermosetting resin.

There are two main characteristics of the prepgs to be considered:

- The tack level, or the stickiness of the prepg, which depends on the resin fraction volume and the degree of polymerization. The adhesion between the layers of the laminate and between the laminate and the mold depends on the tack level.
- The drapability, which refers to how easily the prepg can assume the shape of the mold without causing defects on the final product. It depends, as for the tack level, on the resin fraction volume and on the degree of polymerization. Is usually difficult to produce extremely complex parts using prepg as raw material.

Prepgging can be accomplished in three ways: by hot melting impregnation, by resin filming, and by solvent impregnation (Campbell, 2014). In the hot melting impregnation, the fibers are fed from a creel, collimated, and impregnated with a melted resin and then cooled

before getting spooled on a roll. In the resin filming process, first, the resin is filmed to the desired thickness on a backing paper, then it is applied on the fibers by heated rolls; the combined effects of heat and pressure guarantees the impregnation of the fibers. Nowadays, the filming technique is the most used because it allows better control of resin and fibers content.

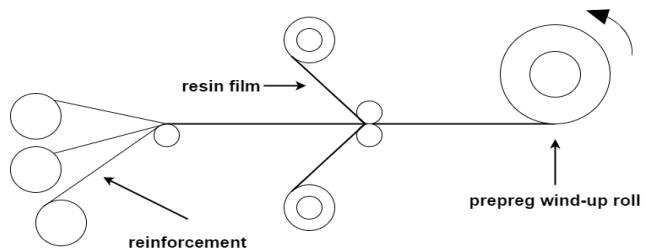


Figure 3. 5 resin filming process

In the solvent impregnation process, the fibers are impregnated in a tank containing a resin solution and then pulled through a set of nip rollers to set the resin content; the fibers are then moved in a hot-air oven to remove the solvent by evaporation and spooled up with a layer of release film. The solvent impregnation has the disadvantage of possible solvent residues in the prepeg which could cause volatile problem during cure. It is a process used for materials like high-temperature resins which are not amenable to hot-melt prepregging. In those processes, compaction rolls are used to achieve an optimum resin distribution. Prepreg rolls must be stored in a cooled area (with a temperature between -15 °C and -20 °C), to avoid the resins to completely cure.

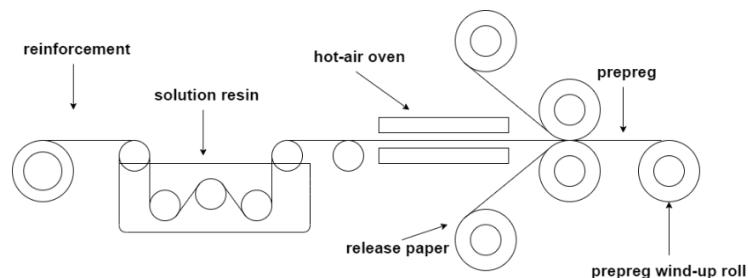


Figure 3. 6 solvent impregnation process

CHAPTER 4

PRODUCTION PROCESSES FOR COMPOSITE MATERIAL

Some of the process used for the production of plastic and composite part are described as follow.

4.1 Compression molding

Compression molding (CM), also called matched die molding, is among the oldest materials processing techniques. It was one of the first industrial methods for molding thermosetting polymers (also called thermosets, TSs) but today it is also used for thermoplastic polymers (or simply thermoplastics, TPs), elastomers (both TS and TP), composites and natural rubbers. In CM, the final product is obtained by heating the raw materials and by applying pressure within a closed mold cavity, so that the resin liquefies and flows, taking the shape of the mold. The viscosity is then increased by means of cross-linking, in the case of TSs, or simply by cooling, for TP. Once the product is sufficiently strong and cold, it is removed from the mold.

The process uses a hydraulic press (or less often a pneumatic press), with heated platens and with a compression capacity between 100 tons and 5000 tons ("Appl. Plast. Eng. Handb.," 2017), depending on the requirements for the part to be made.

The mold consist of two components: the female (or cavity), which is usually mounted on the lower part of the press, and the male (or plunger), which is attached on the upper part and is aligned to match the cavity. These components have to withstand high shear and compressive forces, therefore they are commonly made of are stainless steel, tool steel (which can even be chromed, to improve performance and lifetime), or, for shorter runs and lighter duties, aluminium alloys such as 6061 and 7075.

Some of the most commonly used plastics for CM are phenolics and epoxies resins, silicones, TS and TP polyesters, ureas and melamines; they can also be reinforced, in order to make polymer matrix composites.

Moreover, there are various forms of “premix” of reinforcing fibers, fillers and resins that can be prepared and used for molding, such as prepreg, sheet molding compounds (SMCs), bulk molding compounds (BMCs), preform and mats with liquid resin.

SMCs are composite materials in the form of a sheet, containing about 30-50% of fibers, 25% of resin and 25-45% of filler (Al_2O_3 , CaCO_3 or clay), and small amounts of other ingredients (i.e. additives and thickener). During production, the resin is partially cured to the B-stage and then it is stored in a refrigerated place to avoid complete curing. In the use phase, SMCs sheets are cut to match the product's size. BMC is, instead, a bulky mixture of chopped fibers, resin and fillers, that has a dough-like form rather than a sheet form.

The cycle to obtain the molded part consists of the following steps:

1. Precharge preparation and placement

The raw material (or precharge, or charge) is weighted out and placed in the hot mold. For thick parts, the charge can be preheated. Depending on the type of the mold there can be an excess of material (flash mold and semipositive mold) or the exact amount of material needed (positive mold). The precharge position is a key factor for the quality of the part, since it affects fiber orientation, void content and knit line formation.

2. Mold closure

The plunger moves down and compresses the charge. As the pressure and the temperature increase, the material flows and fills the cavity, causing air to escape. Temperature (typically between 150 and 200 °C), pressure and mold closing speed are the parameters to be considered.

3. Curing/cooling

Once the cavity is completely filled, temperature and pressure are maintained. In case of a thermosetting matrix, this leads to a complete curing (C-stage) and the part is consolidated. For thermoplastic matrix, the consolidation happens after cooling. The curing time depends on the resin type, the part thickness and the mold temperature. The cycle time must be minimized to improve economic efficiency (the recommended compression time is usually between 0,5 and 5 minute). In the case of TSs the part can be removed from the mold once the minimal stiffness is achieved

through cross-linking (hot rigidity), and the polymerization reaction continues out of the mold.

4. Part release

As soon as the resin is cured or has sufficient stiffness, the part is removed from the mold with the aid of ejectors pins. Then the part is cooled down to room temperature, while the mold surfaces are cleaned and treated with a release agent, preparing the tools for the next cycle.

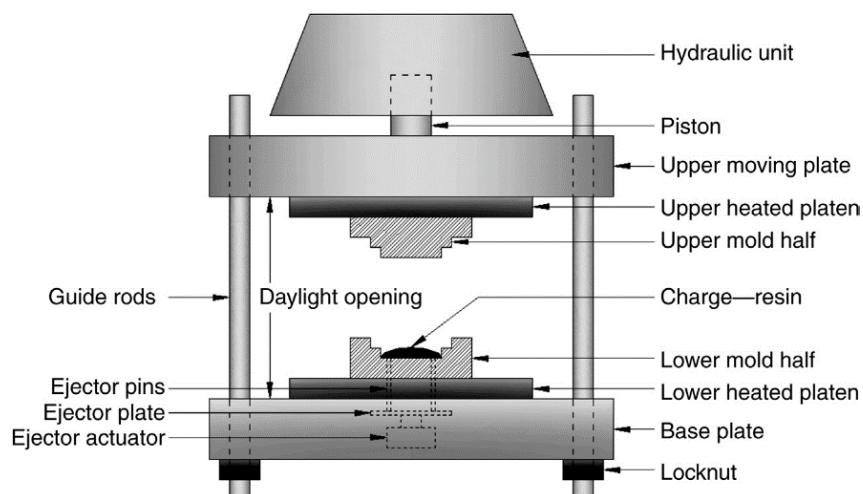


Figure 4.1 compression molding press

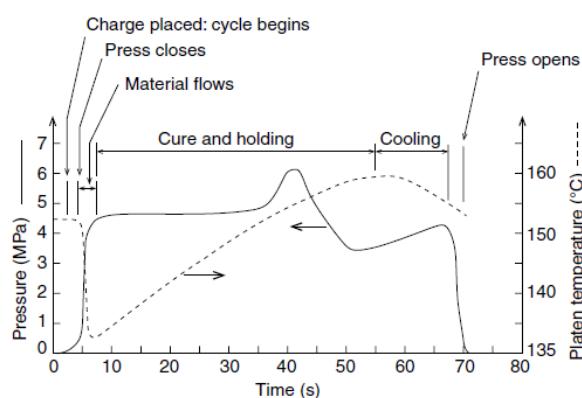


Figure 4.2 temperature and pressure variation during compression molding

CM was the most used method to process plastics during the first half of the 20th century and it is popular even today, due to its simplicity. Some of the other advantages of CM are: low tooling cost , excellent part reproducibility, little material waste; the products have high mechanical properties; it is suitable for a wide range of products dimensions; the clamping pressure required is lower than in most other processes; labour costs are low; complex shapes can be fabricated (but not as complex as with transfers or injection molding ones), the fiber content can be easily controlled; surfaces are finished and high production rates can be obtained (Rosato et al., 2004).

On the other hand, CM requires more equipment than hand lay-up, transparent products cannot be made, and there can be surface imperfections, such as pitting and waviness.,

4.2 Autoclave production

The autoclave processing, also called vacuum bag process, is the method used when high-performance reinforced plastic composites are required, such as in the aerospace or racing sector. It is an open mold process; after a skilled operator has conducted the lay-up phase, a vacuum bag is used to cover the part, and the assembly is placed in an autoclave, where, with controlled pressure and temperature, the resin is cured. The autoclave processing requires long manufacturing time, and the lay-up phase can be object of human placement errors: in fact, researchers are focusing on developing an automated lay-up system, to improve the productivity and the reliability of the process .

The autoclave processing is composed of four main phases:

- 1) Mold preparation
- 2) Cutting
- 3) Lay-up
- 4) Molding and demolding

1. Mold preparation

The procedure for the preparation of the mold can be described by the following steps:

- Cleaning the mold surface
- Application of mold release agents (i.e. wax, Teflon), to facilitate the extraction of the part
- Drying in the oven to create a release film
- Removal of release agent surplus
- Application of gelcoat, to provide high-quality finish and coloured surface of the product.

The material of the mold is chosen depending on the production volume and the dimensional tolerances of the part. For low volume production runs, wood is an option, while for medium or high volume, epoxy resin composites, aluminium or steel are used. When high precision is needed, the mold is usually made of carbon fiber reinforced epoxy resin which, with the right fibers direction, can have a CTE (coefficient of thermal expansion) close to zero.

2. Cutting

The raw material used in this process is usually a prepreg, a thin sheet of fibers impregnated in a polymer matrix. The material is removed from the refrigerated storage and it is kept at room temperature for defrosting. It is then cut in the desired shape, orientation, and dimension, according to the design requirement. This process can be done manually, using of a simple mat knife, or in more automated ways, with laser beams, high-speed water jets or trimming dies.

3. Lay-up

In this phase, the polyethylene (PE) backing paper is removed from the prepreg, and the layers of prepreg are manually stacked to form a component of the desired shape. This can be done in two different ways: with the "ply on ply lay-up" the sheets are stacked and then are positioned in to the mold (preplying), while with the "direct on tool lay-up" the plies are deposited directly into the tool. After each ply is stacked, a preliminary bulking operation removes the air entrapped between the layers. In addition to the prepreg, other structures

can be added to the stack, such as honeycomb cores, pre-cured composites, and structural adhesives.

Once the desired thickness is obtained, the vacuum bag is placed and, thanks to the creation of a vacuum under the bag, air and excess resin are removed from the part. The bag consists of several consumable materials:

- Peel ply

It is a layer of fabric material (i.e. nylon or glass) which is applied directly on the outer surface of the composite. During the cure cycle, the peel ply absorbs part of the resin so that when it is removed it fractures a thin layer of resin, leaving the part with a fresh, clean, roughened surface, ready for the subsequent bonding operation. If required, a second peel ply can be placed between the laminate and the mold, to allow adhesive application on both upper and lower surfaces. (Wegman and Van Twisk, 2012)

- Release film

The release film is a perforated film, usually made of polytetrafluoroethylene (PTFE), used to separate the laminate from the rest of the vacuum stack and to remove air, excess resin and other volatiles from the part. The amount of resin that flows out of the laminate is determined by the cure pressure and temperature, by the rheological properties of the resin used, and by the spacing and size of the perforations of the release film. This flow affects the fiber and resin volume contained in the product and consequently its mechanical properties.

- Bleeder

This layer is made of polyester, glass fibers or cotton, and it absorbs the excess resin that flows out during the molding phase. The manufacturing process of the bleeder ensures that the holes do not close up during the curing due to the pressure applied. Since quantity of resin that can be absorbed depends on the thickness of this layer, the selection of the bleeder is based on the quantity of resin needed in the final product.

The bleeder fabric is designed to have a good elongation in all directions so that it can be draped easily over complex curvatures, avoiding any bridging (<https://www.gurit.com/>).

- Breather

The breather ensures that the air and volatiles can be extracted from the laminate and protects the vacuum bag from the sharp edges of the mold. In most simple vacuum bag

processes, where the laminates are thin and with low resin content, one layer of fabric acts as both bleeder and breather.

- Vacuum bag

The vacuum bag is the last layer, and it is used to seal the whole composite laminate and the vacuum consumables. Many polymer materials can be used to produce the vacuum bag such as polyester, nylon and silicone rubber; if the curing temperature is above 200 °C, a polyamide bag is employed. Sealant tapes are used to seal the vacuum bag to the tool, avoiding that air escapes from the vacuum bag. The tape is composed of a synthetic rubbers blend and inert fillers, plasticiser and tackifiers, to provide the required properties of tackiness, high temperature resistance and chemical resistance.

A plumbing system provides an airtight passage from the envelope to a vacuum pump, allowing the pump to remove the air from the bag and to reduce the pressure up to -800 mmHg. (West System Epoxy, 2010). A countermold can be exploited to provide even better distribution of the pressure on the laminate.

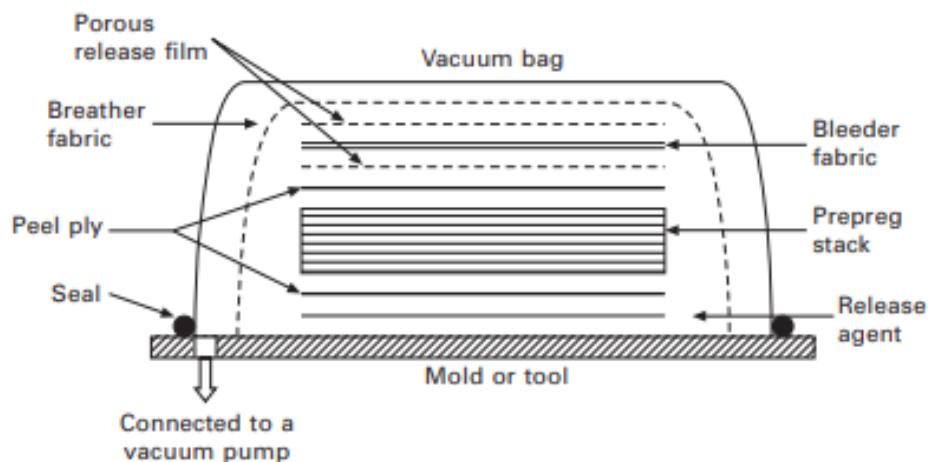


Figure 4.3 autoclave bag molding lay-up scheme

4. Molding and demolding

After the lay-up phase, the assembly is placed inside an autoclave for curing and consolidation. The autoclave is basically a vessel that uses air, steam, nitrogen or Co₂ as a circulating heated gas, to provide temperature and pressure control. Heating can be achieved by electrical heaters or by diathermal oil flowing in an exchange circuit. The combined effect

of the vacuum created inside the bag, the pressure applied in the autoclave and the high temperature, causes compaction of the laminate, air and volatiles extraction and curing of the resin. The curing cycle in the autoclave can be divided into three phases: heating, maintenance and cooling.

Heating: the part is placed inside the autoclave and the temperature slowly increases, with a heating speed that depends on the number of parts inside the vessel and on their thickness. The pressure increases too; depending on the compaction needed for the product, the gas pressure can be between 0,36 and 1380 MPa (Rosato et al., 2004); the higher pressure yields denser products. The vacuum pump extracts air from the bag.

Maintenance: temperature and pressure are maintained till the desired level of curing is achieved.

Cooling: cold air starts to cool the laminate, then the pressure in the autoclave drops and the pressure inside the bag increases. The composite is cooled to room temperature, the autoclave is opened, and the vacuum bag is removed (demolding).

Depending on the resin, the curing cycle may take anywhere from 30 minutes to several hours. The curing cycle in autoclave guarantees an optimum fiber wet-out, the removal of air from the prepreg, the removal of excess resin and the removal of solvents from the resin. The autoclave processing allows to have high mechanical properties, flexibility in fiber orientation, reproducibility and the production of complex shapes; all those characteristics make it a good choice for aerospace industry, for automotive prototypes and for the racing sector. However, vacuum bagging in autoclave is a time-consuming process, especially for producing large components, due to the manual layup phase, the curing cycle and the debulking. It also includes the use of expensive and disposable materials. The heating inside the autoclave is not efficient due to convection, and a large amount of gas is needed for the process; in this conditions it is difficult to predict the exact amount of time needed for the complete curing and usually extra time is wasted.

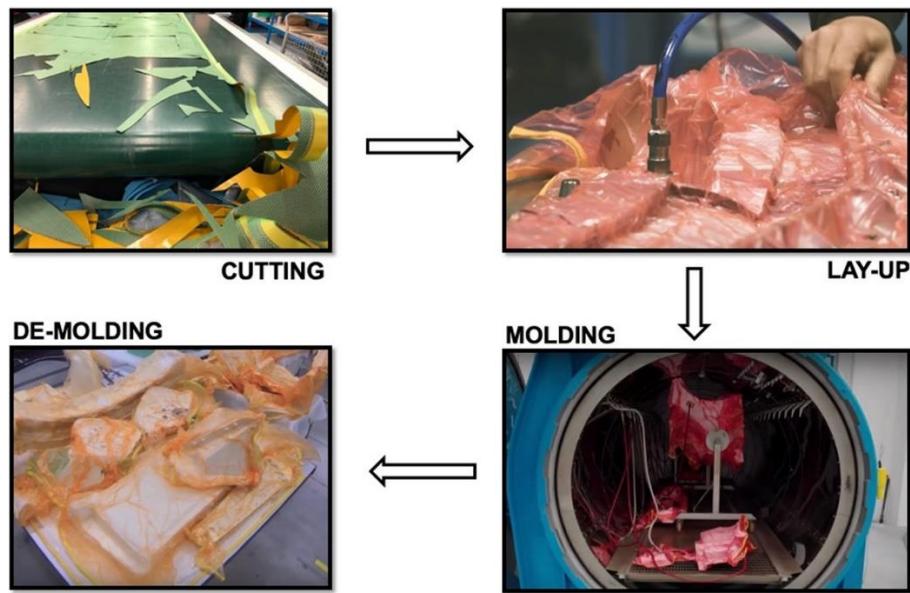


Figure 4.4 main phases of the vacuum bag process

4.3 Injection molding

Injection molding (IM) process has been used for nearly 150 years and nowadays it is used principally for processing unreinforced or fiber reinforced thermoplastics polymers. Even if it is possible to produce TS components by IM, at least the 90wt% of all plastic processed by IM are TPs. The modernization of the IM process began in 1950s and in the 1960s the reciprocating screw injection molding machine (IMM) was introduced. The modern IMMs are composed of two halves: the injection unit and the clamping unit. In the injection unit, the raw material (the molding compound) is introduced in the barrel by a feed hopper. A rotating screw moves the plastic toward the mold while, due to the combined effects of the heat friction generated by the screw and heaters positioned outside the barrel, the material melts. Then the screw, acting as a piston, forces the polymer inside the mold. The clamping unit captures the material into the mold and, under defined conditions of temperature and pressure, forms the finished product.

Figure 4.5 shows a typical injection molding machine.

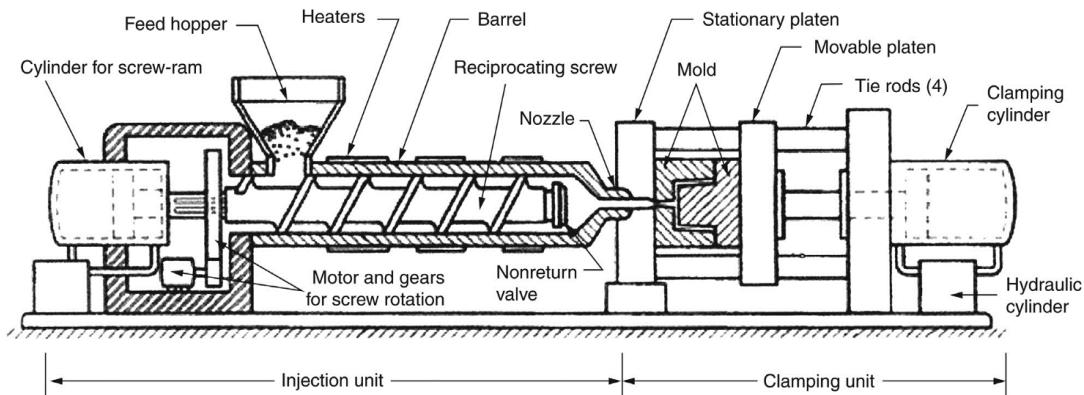


Figure 4.5 injection and clamping units

Injection molding is a cyclical process with cycle times that range from 10 to 100 s. The cycle time is determined by the cooling time of the melted plastic. Figure 4.6 shows the actions occurring during a molding cycle with a Pressure-Time graph:

- 1) The mold is closed by a clamping system and a signal is sent to the injection unit
- 2) The screw moves forward and acts as a piston, causing the melted plastic to flow into the mold cavity. The mold starts to fill and the pressure inside it increases.
- 3) The material flows and fills the cavity. This is done as quickly as possible to minimize the thermal loss from the plastic and to exploit the low viscosity associated with high shear rates in most plastics. The screw keeps applying pressure to compensate for any shrinkage caused by the cooling of the melt polymer.
- 4) A gate, composed by the thermoplastic polymer between the mold and the screw, solidifies and isolates the cavity from the rest of the machine. No more material can be forced inside the mold after the solidification of the gate. As the two halves of the machine are separated by the solidified gate, the screw stops applying pressure and moves backwards. It starts to rotate to mix, melt, and transport the new polymer for the next shot. Meanwhile, the polymer inside the mold cools down and gains rigidity.
- 5) When the part has a sufficient rigidity (in most cases when the glass transition temperature or melt temperature is reached), the mold is opened and the part is ejected.
- 6) The mold closes and the cycle starts again.

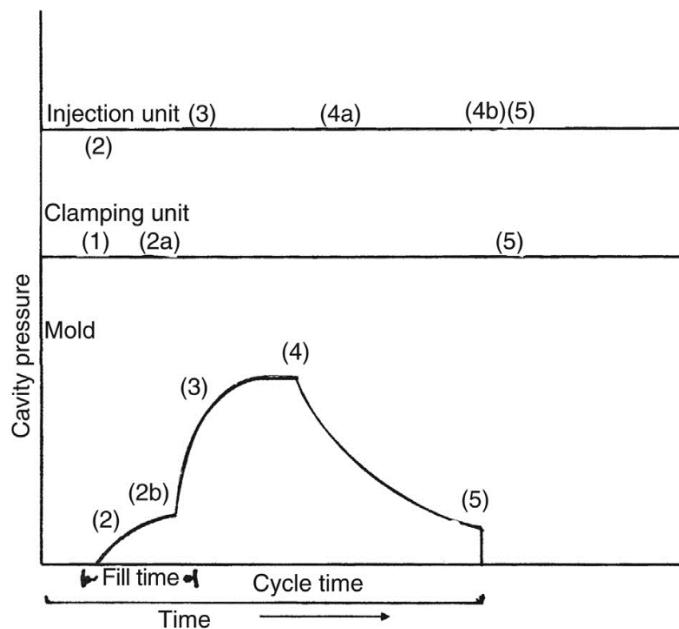


Figure 4. 6 injection cycle pressure-time graph.

IM allows to produce near net shape products and very little post-production work is required. The process is suitable for high volume production as it can be fully automated (Advani & Hsiao, 2012). The raw material used for injection molding production is a blend of different materials. A thermoplastic resin is usually added with either particulate (i.e. talc, CaCO_3 , TiO_2 , etc.), chopped carbon or glass filaments, natural fibers, or other polymers with high modulus. For the reinforced plastics, the short fiber content is typically between 20%wt and 50%wt. Long glass fiber reinforced plastics can be produced too using special machines optimized for those materials.

CHAPTER 5

PREPREG WASTE MANAGEMENT

Landfill and incineration are, nowadays, the most used methods of disposal for composite waste. In 2000, the total waste produced by the composite market was estimated to be 156000 tonnes, of which around the 70% derived from end of life waste, and the 30% derived from production waste (Halliwell, 2006). The CFRP market demand highly increased in the last decades and it is expected to keep increasing. The need for the development of new and environmentally friendly alternatives for the treatment or reuse of prepreg wastes is given by both environmental and economic reasons. Moreover, the European Union legislation on landfill disposal is becoming every day stricter, putting pressure on the traditional methods of dealing with composites waste. The European Commission believes that composites materials cannot be considered to be inert waste from the landfill point of view and, even though landfill of composites is not forbidden yet, landfill taxes provide a big incentive to reduce the quantity of waste sent to landfill and increase the amount of waste processed by the companies in order to lower their environmental load (Marsh, 2003). One example is given by the automotive sector because it is one of the major users of composites and has been an early target of EU legislation.

5.1 Waste hierarchy

The European Directive 2008/98/EC, or Waste Directive (amended from the original directive introduced in 1975, Directive 75/442 EEC), establishes some of the key criteria on waste management. According to this directive, wastes must be managed without endangering human health and harming the environment, without risk to water, air, soil, plants, or animals. Article 3 of the directive defines the “waste hierarchy”, a series of options for dealing with waste, listed in order of preference. The hierarchy, from most desirable to least desirable options, consist of:

- Prevention
- Reuse

- Recycling
- Recovery
- Disposal



Figure 5. 1 waste hierarchy

5.1.1 prevention and waste minimization

Prevention is about minimizing waste through the efficient use of raw materials and energy. It is also known as process or resource efficiency since it is achieved by understanding and changing processes to prevent waste production. For example, waste minimization is achieved by designing a product that has low environmental impacts during production and use phases. In this case, the Design for Environment can be a useful tool to lower the environmental load associated with a product. Prevention can provide several benefits to business:

- Cost saving

Improving the resource use efficiency, the production costs can be reduced

- Compliance

To reduce the possibility of litigation

- Risk reduction

- Market positioning

Through the production of eco-friendly products

5.1.2 Reuse

Reusing composite parts after the EoL of a product is high in the waste hierarchy but it is not the most practical option for many composites' applications as there can be some issues associated with materials re-use. The first issue regards the properties of re-used composites components. For components used in external applications, surface degradation may occur, while for structural components the re-use may be impossible due to the difficulties to calculate the load-carrying properties as a recovered item. Another problem to deal with is the re-certification of composite products that may be expensive if testing is involved. From the producer point of view, manufacture a new product may be less expensive than re-certificate it. The demanufacturing process must be taken into account during the design phase to facilitate the deconstruction of the product and the re-use of its components (design for demanufacturing). Otherwise, the dismantling process can be difficult or even hazardous for the deconstruction staff, for example, because of dust exposure.

5.1.3 Recycling

Composite wastes need to be recovered in as clean as possible condition to make recycling procedure easy and cost-effective. Composites are often used in association with other materials, even jointed together by adhesive or mechanical means; it follows that sorting and obtaining clean parts may results difficult. Currently, most of the sorting is still done by hand, resulting in an expensive and time-consuming process. New technologies to automatically sort polymers are being developed and introduced. These technologies may include, for example, shredders and hammer mills to break up the waste, magnetic separators to remove ferromagnetic particles, current separators to remove nonferrous metals, air stream, hydrocyclones and centrifuging to separate particles with different density, and electrostatic separation or organic solvents to separate different types of polymers. A labelling system allows rapid identification of the waste type and makes the recycling process easier.

There are essentially four classes of recycling technique:

- Primary recycling
- Is the production of a recycled product with similar mechanical properties of the original material.
- Secondary recycling

Is the creation of a material with lower properties than the original material.

- Tertiary recycling

Is the conversion of the wastes in chemicals and fuel.

- Quaternary recycling

It consists in the incineration of the wastes to obtain heat energy. Some do not consider it as recycling but rather as a recovery process.

From the point of view of material utilization, the first two levels of recycling are preferable.

From the point of view of economic and environmental impacts, this may not be true: for example, the preparation processes for secondary recycling may require a big amount of energy and other resources, making the recycling not effective and environmentally friendly.

Several primary and secondary recycling techniques consist of mixing some waste material with virgin raw material and use the blend as if it were all virgin material. The recycling processes of composites can be classified in four main categories:

- Thermal recycling
- Mechanical recycling
- Chemical recycling
- Radiation based recycling (Howarth et al., 2014)

5.1.3.1. Thermal recycling

Thermoplastic matrix composites can be recycled directly by heating, remelting, and remoulding them, obtaining a high value recycled material (Goodship, 2010). The recycling process for thermosetting matrix composites is much more difficult as they cannot be remoulded. In a fiber-reinforced polymer, the most valuable constituent is usually the reinforcement, particularly in the case of CFRP. Several recycling processes aim to recovery high-grade fibers from the scraps of used composite parts, such as in the case of the fluidised bed thermal recycling process. Fluidisation is a process in which a bed of solid particles is transformed into a fluid-like state through suspension in a fluid, usually gas. The gas pass through a porous air distributor plate where the solid particles rest. The plate is inside a containment vessel. With high gas speed, the solid particles suspend and start to behave as a fluid. In the recycling process, the fibers are recovered from the composites by removing the matrix by heat in a bed fluidised with air. A gas-solid separation device (i.e. a cyclone),

separates the fibers from the polymer. Then the gas stream passes in a secondary combustion chamber to fully oxidise the polymer. Heat can be recovered from the high-temperature exhaust gasses and any pollutants can be scrubbed before being emitted to the atmosphere. Figure 5.2 shows a simplified diagram of this recovery process.

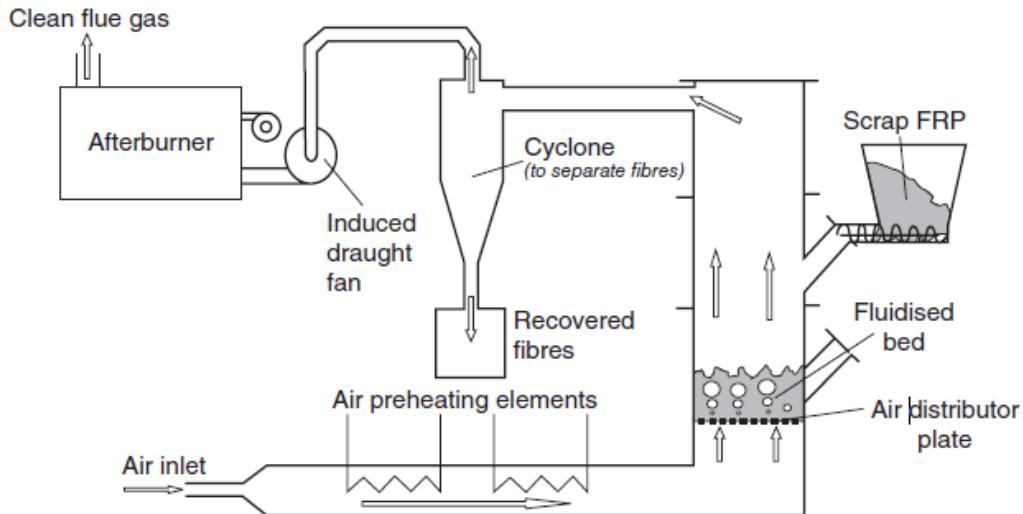


Figure 5.2 fluidised bed recycling process

The scraps are prepared before the recycling process by chopping them (for example with a granulator), to reduce their size. The fluidised bed process recovers fibers in form of short individual filaments no longer than 30 mm. The limited length is needed to prevent agglomeration during the process and to avoid material handling and processing problems during reuse of the fibers. The process has the advantage of being tolerant to mixed and contaminated materials, so it is suitable for recycling composite waste from end-of-life product. The energy consumption associated with the fluidised bed recovery process for CF, according to a study of Meng et al (Meng, Olivetti, et al., 2018), is 6 MJ/kg for the parameters considered in that study. In comparison with the production of virgin CF, which has an energy requirement ranging from 198 to 595 MJ/kg, the recovery process guarantees a considerable energy saving.

Pyrolysis is another process suitable for recycling polymer composites. It is a thermally initiated chemical process that decomposes the organic molecules to smaller one in an inert atmosphere. The thermal decomposition products of the polymer matrix evaporate, and the reinforcement material can be recovered and reused. Moreover, the matrix phase can be recovered as feedstock chemicals.

5.1.3.2 Mechanical recycling

Mechanical methods are the most mature technique available for CFRP recycling and they are suitable for both domestic and industrial waste. As for thermal methods, the waste must be sorted, granulated, and prepared for the end application use. The wastes are sorted on the basis of the polymer fraction, then a granulation step reduces the composites to a manageable bulk density before further separation processes. During the size reduction processes, the wastes are shredded and granulated by a rotatory cutting system to a size of approximately 3,2-9,5 mm. If the recycled wastes are composites with fibers reinforcement, the granulation phase will result in mechanical damages for the fibers, reducing considerably their length. However, those fibers can be used as fillers in re-manufacturing. A study from Howarth et al (Howarth et al., 2014), valued the energy consumption associated with the recovery of short carbon fibers from continuous unidirectional carbon fiber/ epoxy resin prepreg to be between 0,27-2,03 MJ/kg, showing that this recycling process brings environmental benefits.

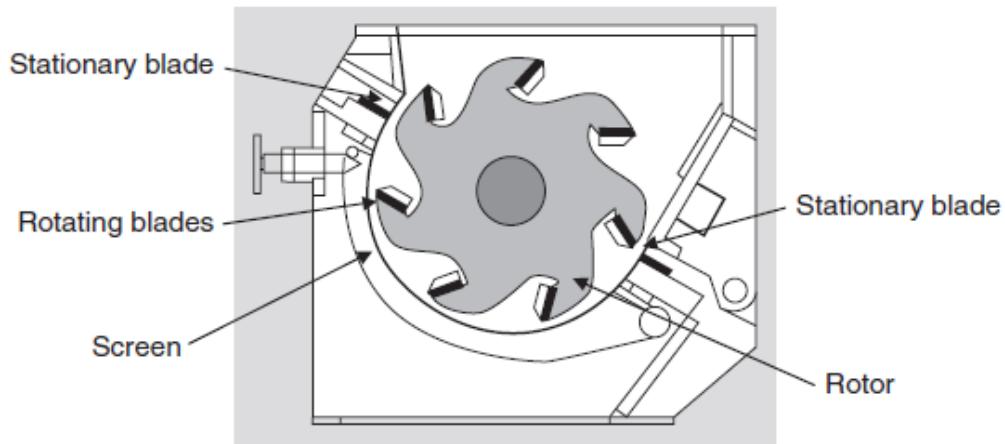


Figure 5. 3 schematic cross section of a shredding recycling machine

After the granulation, the materials are washed and sorted into their individual generic types so they can be prepared for further processing. Before reusing or selling the recycled material, it is often re-formed to give it a consistent appearance, to blend the material with a virgin compound or to add additives to improve the performance of the material.

5.1.3.3 Chemical recycling

Chemical recycling usually consists in the separation of the fibers from the matrix by mean of a reactive medium, for example, a super-critical fluid. For example, Jiang et al presented a study where carbon fibers were recycled using supercritical n-propanol in a semi-continuous flow reactor (Jiang et al., 2009).

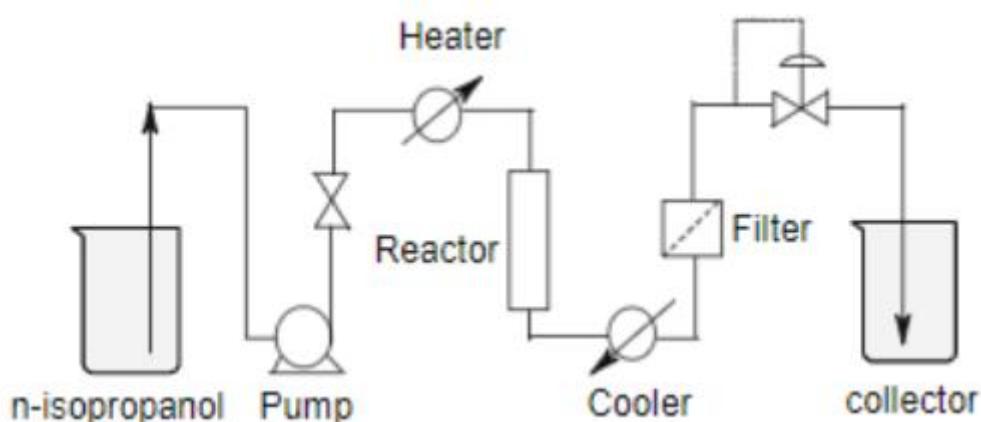


Figure 5. 4 simplified scheme of a chemical recycling process

The carbon fiber/epoxy resin prepreg scrap was inserted in a tube reactor where heated n-propanol was pumped. The fluid fully decomposed the epoxy resin and, as the system cooled down, the carbon fibers were collected, cleaned, and dried to prepare them for future uses. The study results showed no significant reduction in the mechanical properties of the fibers. A decrease of the surface oxygen of the carbon fibers was observed. This leads to a reduction of the interfacial bonding strength with epoxy resin.

5.1.3.4 Radiation based recycling

Radiation-based methods, such as microwave pyrolysis and thermolysis, have been researched as possible recycling options for CFRP. In the microwave thermolysis process, CFRP wastes are heated by a microwave system in a furnace cavity, where oxygen is pumped

continuously. At a sufficiently high temperature, the matrix decomposes completely, allowing the fibers to be recovered.

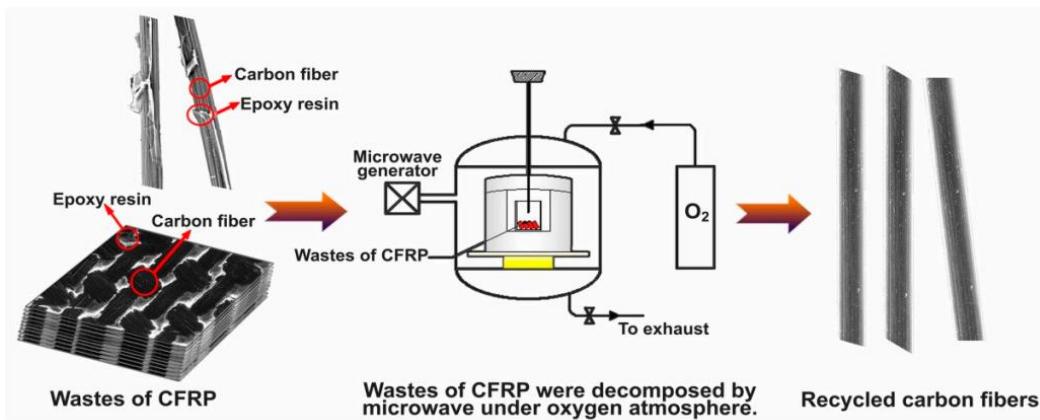


Figure 5. 5 simplified scheme of a radiation-based recycling process

A Deng et al study (Deng et al., 2019) regarding the microwave thermolysis recycling method on carbon fiber/epoxy resin prepreg waste, showed that this method is faster and more efficient than the traditional thermolysis (time was reduced by 56,67% and the recovery ratio increased by 15%). Additionally, the fibers' surface was cleaner, smoother, and contained less epoxy resin in the microwave process. However, when this system is used at the same reaction temperature as that of the traditional method, microwave heating has an influence on the chemical structure of the fibers, altering their graphitization degree.

5.1.4 Recovery

Quaternary recycling, or recovery, usually consists of the conversion of waste into energy by mean of a combustion process: the incineration. There are different types of incineration processes (i.e. grate incineration and rotatory kiln) which are chosen depending on the volume, type, and hazard of the waste to be destroyed. The calorific value depends on the inorganic content of the waste. Natural-fibers reinforced polymers are thought to be the best type of composites for incineration as both the natural fibers and the fillers should burn easily leaving no residue. Other types of composites, for example, glass fibers reinforced polymers, leave residues after the process because some elements (i.e. the glass fibers) may not burn. For a typical GRP (glass reinforced polymer) product, the residue after incineration is around

70% of the composite (Buggy et al., 1995). Another problem is that the fibers do not simply burn out but shatter into fragments that can be carried out from the hot zone via thermal convection and can cause health, safety, and performance issues. Combining incineration with cement production is a better option to deal with composites wastes as, in addition to the energy recovery, the unburnt materials became part of the cement, resulting in material recovery. However, incineration is not a good long-term solution for dealing with the EoL of composites materials. An LCA analysis, conducted by Meng et al (Meng, Pickering, et al., 2018), showed that, even considering the energy saving, the incineration process has a net GHG (greenhouse gasses) emission of 2,14 kg CO₂ eq/kg CFRP waste, mainly because during the combustion process the carbon content of the composite material is released to the environment as CO₂.

CHAPTER 6

LIFE PROGRAMME AND CIRCE EUROPEAN PROJECT

6.1 LIFE programme

The LIFE Programme (from french: L'Instrument Financier pour l'Environnement) is the European Union's (EU) funding instrument for the environment and climate action. LIFE objective is to contribute to the implementation, updating and development of EU environmental and climate policy and legislation by co-financing projects with European added value. It began in 1992 and, since then, it has co-financed more than 5,400 projects with a total contribution of approximately 6.5 billion Euros.



EU took measures to limit pollution and improve waste treatment since 1972; in the early 1980s, it started to give financial assistance for nature conservation. In 1982 the European Parliament introduced a small budget line for nature conservation. During those years, the awareness about environmental problems grew rapidly, also due to large scale environmental disasters, such as the Chernobyl incident. Therefore, issues such as the ozone layer depletion and global warming started to be taken into account by the European Union. In the middle of 1980s, the ACE (French: Action Communautaire pour l'Environnement) financial instrument was created to support the development of new clean technologies, new techniques for monitoring the natural environment and to help to protect habitats and endangered species. The total investment of this project was ECU (European Currency Unit)

98 million, divided for 53 nature protection projects and 55 clean technology projects, between 1994 and 1991. Meanwhile, two other supporting environmental programmes were running in two specific regions: MEDSPA (Mediterranean, from 1986 to 1991), and NORSPA (Northern European Maritime regions, from 1989 to 1991). Those two financed projects that regarded water resources, prevention of water pollution, waste disposal and conservation of habitats and endangered species. After the ACE programme ended in 1991, the ACNAT fund for nature was adopted, with goals in the field of habitat conservation. ACNAT was quickly substituted in 1992 by an all-encompassing environmental fund: LIFE.

LIFE I ran from 1992 to 1995 and funded 731 projects focusing on:

- Promotion of sustainable development and quality of the environment
- Protection of habitats and nature
- Administrative structures and environment services
- Education, training, and information
- Actions outside EU territory (third country assistance)

LIFE II covered the period between 1996 and 1999. It was split into three categories: LIFE-Nature, dedicated to mature and conservation actions, LIFE-Environment, dedicated to the implementation of EU environmental policy and legislation, and LIFE-Third countries, which founded actions in countries on the shores of the Mediterranean and Baltic seas. The programme's budget was increased compared to the first phase, reaching a total value of ECU 450.

LIFE III ran till 2006, with an increased budget of € 640 million. It continued the goals of LIFE II. The fourth phase, LIFE+, ran from 2007 to 2013, with a budget of € 2.143 billion. It was split into 3 categories: LIFE+ Nature and biodiversity, LIFE + environmental Policy and Governance, and LIFE+ information and communication. The current LIFE programme (LIFE 2014-2020) has a budget of € 3.4 billion and it is divided into two sub-programmes: one is for the environment and represents the 75% of the financial investment, and the other is for climate action, which represents the remaining 25% of the financial envelope.

During its activity, LIFE programme developed hundreds of green solutions. For example, it helped to improve the quality of the air, to make hundreds of Europe's cities greener. It developed clean technologies in hundreds of industries and supported new practices in the

agricultural field. It developed monitoring techniques for sustainable forest management and to tackle air pollution(<https://ec.europa.eu/easme/en/life>).

6.2 CIRCE project



CIRCE (Circular Economy Model for Carbon Fibre Prepregs) is a project born within the LIFE programme. It started on 01/09/19 and it is scheduled to end on 31/08/22, with a total duration of three years. The goal of this project is to set-up a circular economy model for uncured carbon fiber reinforced polymer (CFRP) prepreg scraps. The ideal objective is to reach a 100% valorisation of this waste by transforming it into a useful secondary raw material for different production systems.

Uncured prepreg scraps can typically derive from two sources. The first is source is generated during ply cutting operations in the forms of off-cuts, trim waste, and end-of-roll waste. Those scraps are usually randomly sized and shaped pieces. The efficiency of the nesting varies depending on the complexity of the shape of the product to be made; typically, the scraps quantity can range between 20% and 50% of the prepreg used. The second source consists of material that lost their properties, for example for out-life or freezer life prepgregs, which are usually in the form of partially used prepreg rolls (Nilakantan & Nutt, 2015). The present study focuses mainly on the first type of prepreg waste. At present, the scraps produced by the involved companies end up in landfill or incinerators, with repercussions in term of pollution.

CIRCE aims to:

- create useful and economically affordable applications where the scraps can be used.
- Develop and industrialize a new process to prepare the prepreg scrap and make them reusable for new production.

- Create new recovery products (i.e. toe caps, reinforcing ribs, carbo-ceramic brakes) with the same mechanical properties of the parts that would have been made with virgin materials. Economic benefits for the involved companies are expected too.

The project is based on the partnership of five Italian companies operating in the fields of research and development and industry.

HP Composites, created in 2010, is word leader in the designing and production of carbon fiber components for the motorsport, aeronautics, naval, and automotive sectors. It is located in Ascoli Piceno (AP), in central Italy. During the peak production periods, it reaches 600 employees. HP offers innovative technologies for the CFRP market and it is the coordinating beneficiary of the project.



Alci develops customized machineries and production lines for rubber, pharmaceutical, food and chemical industries. It has two factory sites in Ascoli Piceno and Lucca.



Base protection creates work footwear. It is based in Barletta (Puglia).



Cetma is a Research and Technology Organization (RTO) based in Brindisi that deals with advanced materials (composites, polymers, bio-based and recycled), ICT (development of specialized software for engineering, manufacturing and services) and product development.



Petroceramics S.p.a., based in Stezzano (Bologna), has a decennial experience in the field of ceramics and composites.



By the end of CIRCE, 10 ton/years of CFRP prepreg are expected to be recovered, avoiding them to be sent to landfill or incinerator, reducing CO₂ emission by 500 ton/year and the energy consumption by 300000 kWh/year. The continuation of the project will be the development of a CFRP prepreg Collection and Recycling Centre (CRC). The business partnership will be extended at first with local firms which deal with CF and then it will be extended from the national market to the European and international market. In this way, 3 years after the end of the project the following benefits are expected:

- 5000 ton/year of CFRP prepreg recovered
- CO₂ emissions reduced by 250000 ton/years
- Energy consumption reduced by 150GWh/year

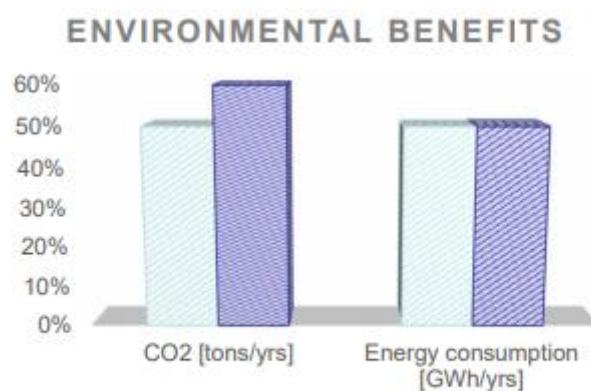


Figure 6. 1 expected environmental benefits by the end of the CIRCE project and 3 years later

The project will ensure costs reduction for the involved companies and will create new job positions.

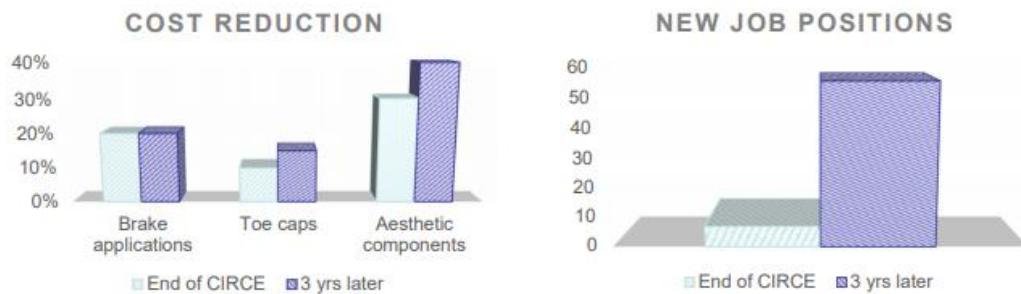


Figure 6.2 expected cost reduction (left) and expected new job position created by the CIRCE project (right)

The processes developed within the CIRCE project will meet all legal requirements regarding industrial emissions (directive 2010/75 on Industrial Emissions) and waste treatment (Waste Framework Directive 2009/98). In fact, CIRCE will improve the recycling and reuse of secondary raw materials through circular economy value chains, improving the environmental behaviour of CFRP products.

The total investment on this project amounts to 2.278.694 € of which 1.180.681 € are co-funded by the European Commission.

6.2.1 CIRCE scenarios

The recovery process developed within the CIRCE project consists of the use of two new machines for the preparation of the prepreg scraps obtained from the cutting process of fabric prepgs. The recovery material will be produced by HP composites. A first new machine is a cutting machine used to cut the scraps in small pieces of around 5x5 cm. The size and shape of the cut scraps may vary depending on the previous cutting operations done on the prepreg rolls. The second machine is a peeling machine used to peel off the PE release paper from the prepreg scraps. In this way, the prepreg scraps are ready for new production processes. If the scraps are not used immediately afterwards those operations, they must be stored in a refrigerated place to avoid the curing of the resin. The virgin material considered in this study is a fabric prepreg composed of long carbon fibers embedded in an epoxy resin

matrix. A blend of preprints with different weight can be recovered and used for the production of new recovery products.

The preparation process turns the virgin long-fibers fabric prepreg waste in short-fibers fabric small pieces of prepreg. It follows that the mechanical properties of the recovery material are lower than the mechanical properties of the virgin material.

Figure 6.3 shows the paths of the prepreg scraps considered in this study. Before the CIRCE project began, all the scraps were destined to landfill, as shown in scenario 1. Thanks to the development of the two new machines, the scraps can now be used for new production processes.

The second scenario concerns the production of a CFRP recovery products by HP composites. At the present time, for research and development purposes only, HP has produced a recycled CFRP sample. The sample was produced using the prepreg scraps in a CM process. In the upcoming future, new parts destined to the automotive sector will be produced using the prepreg scraps.

The third scenario deals with the production of toe caps, used by base protection for the production of work footwear. The toe caps are currently produced by a Base supplier by mean of an injection molding process with a thermoplastic polymer. CETMA is evaluating the technical and economic feasibility of a CM process to produce the toe caps with the prepreg scraps.

The fourth and last scenario concerns the use of the prepreg scraps for the production of carboceramics brakes. Petroceramics uses a PIP (polymer infiltration and pyrolysis) process to produce ceramic matrix composites (CMCs). The first phase of the PIP process is the shaping of the green part by CM using a patented resin system composed mainly by phenolic resin. Petroceramics research and development unit is testing the substitution of a percentage of the phenolic resin with cured prepreg scraps.

In the next chapters, an evaluation of HP Composites and BASE protection production processes is carried out using Life Cycle Assessment analysis.

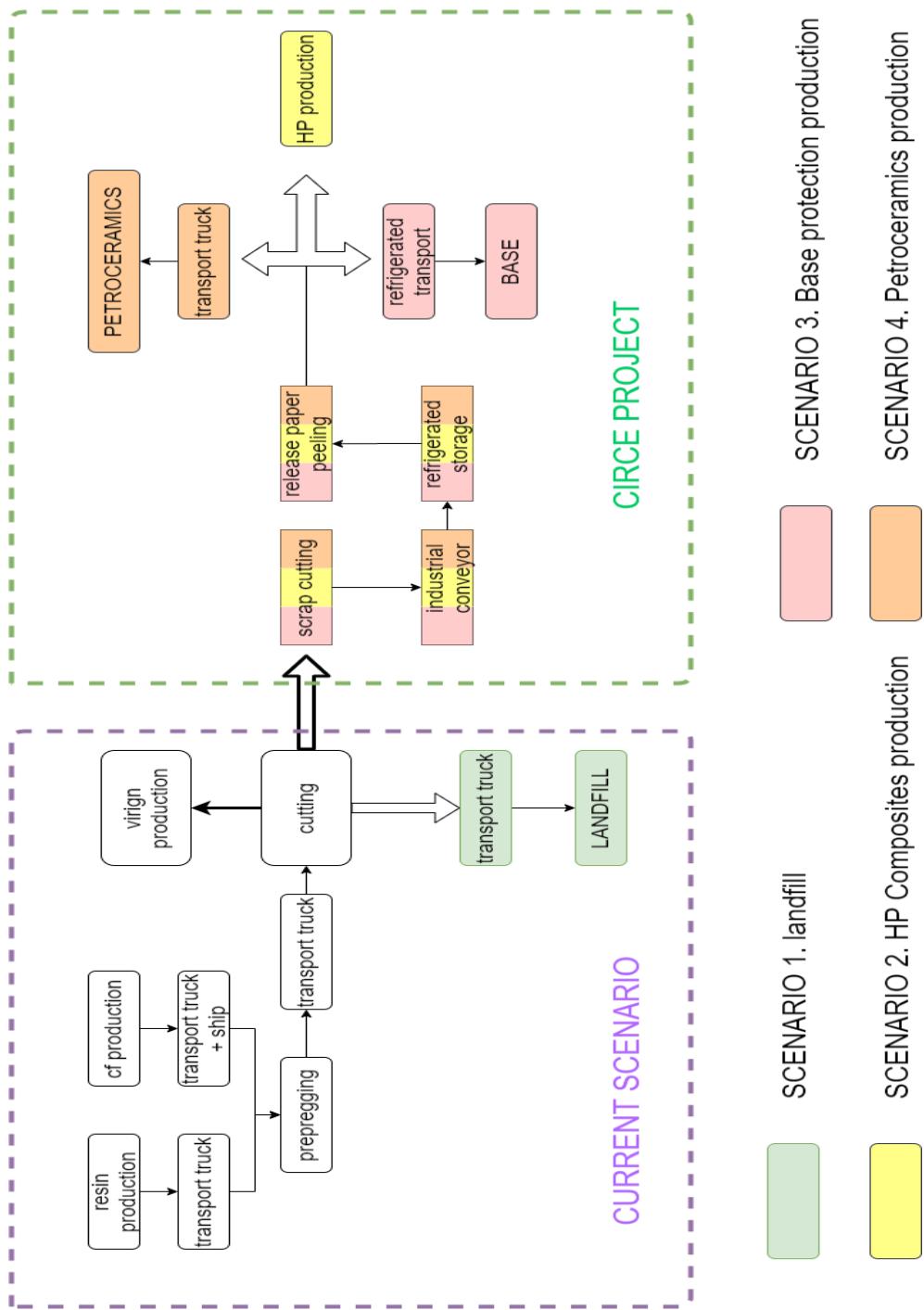


Figure 6. 3 scenarios considered within the CIRCE project

CHAPTER 7

HP COMPOSITE LIFE CYCLE ASSESSMENT

The first LCA analysis presented in this study regards the production of a CFRP prototype by HP Composites. The methodology defined by the ISO standard (ISO 14040-14044) and described in chapter 2, has been followed. In the next paragraphs, the four phases of the LCA (goal and scope definition, life cycle inventory, life cycle impact assessment and, results interpretation) are presented.

7.1 Goal of the study and functional unit

This analysis aims to quantify and compare the different environmental impacts for the production of a CFRP sample through different production processes. This study is collocated within the Circe project, so it follows the LIFE programme objectives. More in detail, this analysis wants to establish if the new prepreg scrap recovery system, specifically designed for the Circe projects, provides a reduction of the environmental load associated with the production of CFRP parts. Moreover, the economic performances of the different scenarios are analysed too. The reduction of environmental impact must not influence the mechanical performances of the part, which must be unchanged.

The functional unit (FU) has been defined as the manufacturing of one unit of the CFRP sample. It has an upper surface area of 0,056 m², a lower surface area of 0,057 m² and it can withstand a tensile load between 5,0 and 5,7 kN. Its thickness and weight vary depending on the raw material used. Productions from prepreg scraps and virgin prepreg rolls were considered. Since the mechanical properties of the recovered prepreg are lower than the virgin prepreg, in order to have the same mechanical behaviour for the parts realized in the different scenarios, the productions from virgin prepreg need a lower amount of material. The sample constituted of recovered prepreg scraps was actually produced by HP composites. It has a thickness of 0,8 mm and a weight of 0,07 kg. Figure 7.1 shows the results of the tensile tests for the recovered prepreg samples. The weight of the sample composed of virgin prepreg has been estimated to be 0,06 kg. The estimation was based on a previous simulation analysis.

Three different scenarios have been considered to simulate different realistic cases:

- Scenario 1
Compression molding production with virgin prepeg.
- Scenario 2
Compression molding production with prepeg recovered scraps.
- Scenario 3
Autoclave production with virgin prepeg.

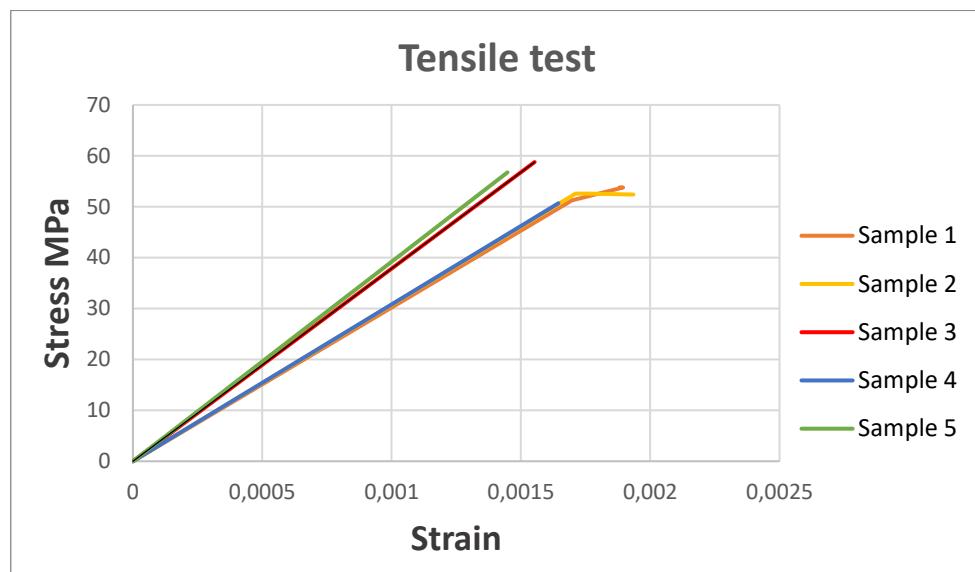


Figure 7. 1 Tensile tests on CFRP recovered scraps samples

7.1.1 System boundaries and scenarios description

The Life Cycle Assessment carried out can be classified as “cradle to grave” as impacts from the extraction of raw materials to the disposal of the final product are considered.

The following elements have been considered in the study:

- Raw materials extraction.
- Materials manufacturing phases.
- Material transport for the prepeg and aluminium tools. For the consumables (i.e. the release agent) the transport was not considered as their limited weight and quantity would lead to irrelevant environmental contribution for their transport.
- EoL (End of Life). The aluminium tools are recycled. The prepeg wastes are sent to landfill. The disposal of the final product is considered because its weight changes in

the different production systems, so the environmental impact of the disposal phases will be different in the three scenarios.

- Production phases.

The use phase of the product is not taken into account. The weight of the analysed part does not influence its use phase so, even if the three scenarios lead to different product weights, the impacts associated with their useful life are considered the same.

- SCENARIO 1. Compression molding production with virgin prepeg

The first scenario regards the production of the CFRP sample through a compression molding process with virgin prepeg. The prepeg is made of high-strength carbon fiber fabric and epoxy resin (the production process of the prepeg has been explained in chapter 3). After the production and transport, the prepeg is stored in an industrial refrigerator. When it is needed, the prepeg is taken out from the refrigerator and cut in the desired shape by a computer numerical controlled (CNC) cutting machine. After the cutting phase, the rest of the prepeg roll is put back in the refrigerator while the prepeg scraps produced during the cutting operation are destined to landfill disposal. The release paper of the prepeg to be used is peeled off by an operator. Then the templates are stacked manually on an aluminium mold (lay-up phase). The mold and the counter-mold are previously coated with a release agent to facilitate the extraction of the part. The aluminium tools are machined through a 5-axis CNC machine. The part is cured due to the application of pressure and heat under a press.

- SCENARIO 2. Compression molding production with recovered prepeg scraps

The second scenario concerns the production of the functional unit through a new prepeg recovery process. The prepeg scraps, which derive from the cutting phases of other virgin productions, are collected and put in an industrial refrigerator to avoid the complete curing of the epoxy resin. When needed, the scraps are taken out from the storage and prepared for the molding process. The preparation system for the prepeg wastes is based on the use of two new machines. A cutting machine is used to cut the scraps in small pieces of about 5x5 cm; the shape and size of those pieces may vary depending on the previous shape of the prepeg waste. After that, a peeling machine is used to remove the polyethylene release paper from the scraps. The following phases are very similar to the standard compression molding production. As in the first scenario, the mold and the counter-mold are coated with

a release agent and the peeled scraps are placed into the mold cavity. Complete curing is then achieved by mean of the application of heat and pressure under the press. The scraps have lower mechanical properties in comparison with the virgin fabric prepreg. Since the different products considered must have the same mechanical performances, the quantity of raw materials needed in this scenario is higher than the previous one. This leads to heavier molds, higher energy consumption for the curing phase and longer labour time (the longer labour time depends on the scraps preparation too). The environmental impact of the prepreg wastes input is considered negative because the reuse of the wastes prevents them from being sent to landfill.

- SCENARIO 3. Autoclave production with virgin prepreg

The third scenario describes the production of the prototype through an autoclave molding. The steps of this process have been already explained in chapter 3. In previous literature analysis (Vita et al., 2019), the autoclave processing with an aluminium mold has shown better environmental performances in comparison with autoclave processing with composites mold. To compare the production from scraps with a good environmental alternative, an autoclave processing with aluminium mold has been considered in this study. Indeed, aluminium molds, which have different thermal distortions from the prepreg preforms, may lead to low geometrical quality of the parts. However, for the considered product, dimensional and geometric tolerances are not crucial. The quantity of virgin prepreg needed for this scenario is the same as in the first one. The cost for the aluminium tool for the autoclave processing is considerably lower than the other two cases because in this scenario an aluminium counter-mold is not required.

Figure 7.2 shows all the phases considered in the three scenarios.

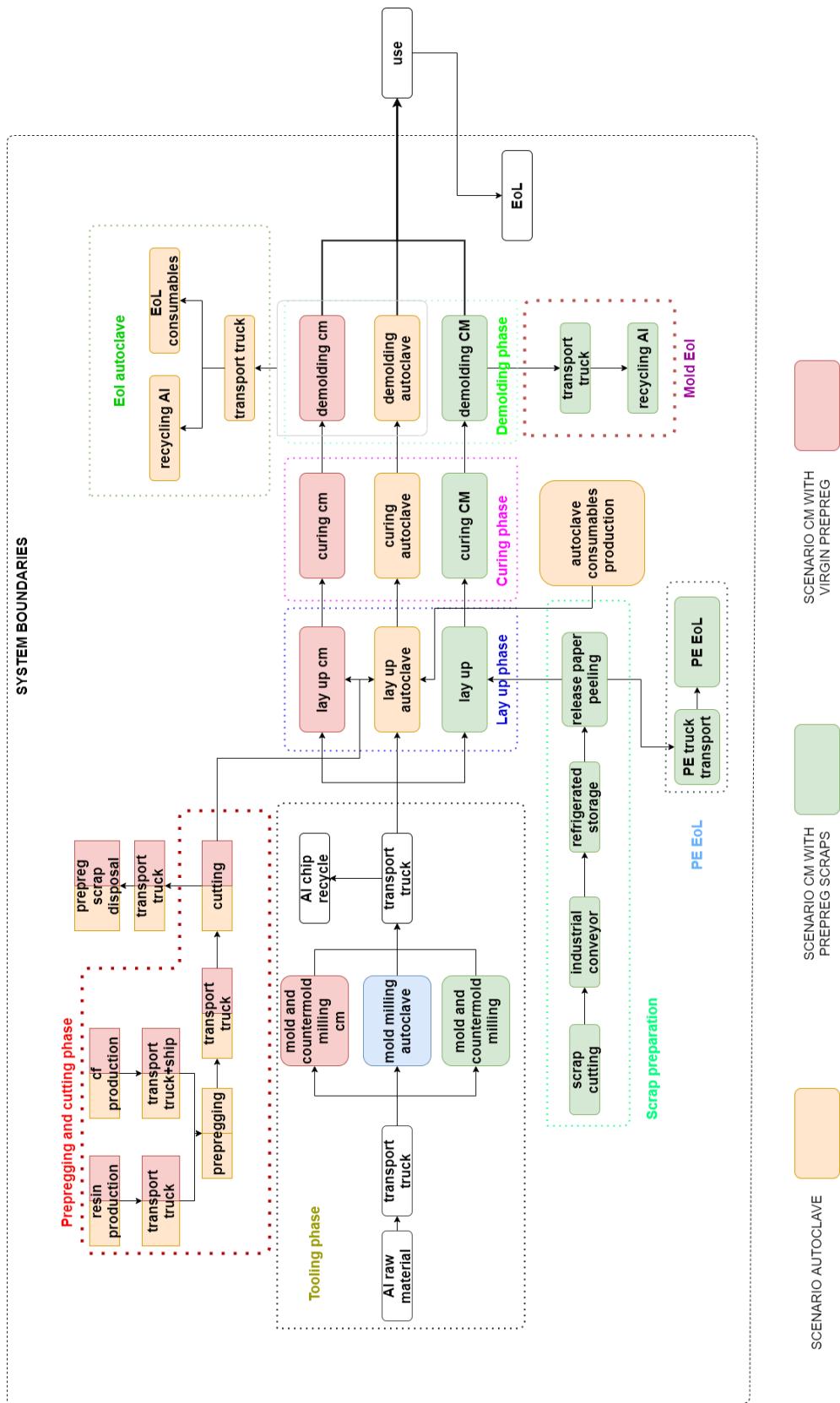


Figure 7. 2 The three scenarios considered in the LCA analysis

7.2 Life cycle inventory

This LCI considers the inputs and the outputs of all the processes with relevant environmental impacts included within the previously defined system boundaries.

The inventory data of this study were collected from different sources. Primary data were collected by direct measurements of the involved company. Secondary data were retrieved from literature research and a commercial LCI database. In particular, the Ecoinvent 3.1 database has been used.

The following assumptions have been made for the collection of the inventory data:

- Data related to input materials of the second scenario have been measured for the actual production process.
- The energy consumption of the press for the second production system has been estimated considering the weight of the molded part.
- Data related to the equipment (mold and countermold) of the second scenario have been calculated on the basis of the component and the equipment 3D models.
- Since the first and third scenarios have not actually been realized, the data related to their input materials, consumables, tools, labour time, and energy consumption and have been estimated. The estimates were made on the basis of literature research and comparison with the second scenario data.
- The energy consumption for the milling phase of the molds has been derived from the Ecoinvent database.
- Other data related to energy consumption have been estimated from aggregated data.
- Inventory data related to input materials have been derived from the Ecoinvent database.
- For the manufacturing of CFRP prepreg, currently, there are no inventory data available within the Ecoinvent database. For this reason, for the prepreg production, it was used the same model developed by Forcellese et al., based on previous literature studies (Forcellese et al., 2020).
- Inventory data related to electric energy generation have been derived from the Ecoinvent database.

- Distances for the considered transportation phases have been estimated by considering the locations of HP suppliers.
- Inventory data related to transportation have been derived from the Ecoinvent database.
- Impacts related to the scraps input are considered negative as their use prevents materials to be sent to landfill.
- In this study, the impacts related to the production of all the machines used (i.e. the autoclave, the press, and the refrigerator) to produce the part are not considered. The useful life of those machines is much longer than the time needed to produce the part, so their manufacturing process inputs are negligible.
- The useful life of the product is not considered as it can be assumed that there are no differences in the use phase for the three scenarios.

In the following paragraphs, all the inputs considered in the study are detailed.

7.2.1 Input material

The main input material used for the production of the sample is the prepreg. The first and third scenarios use virgin prepreg. The nesting efficiency for the cutting phase has been considered equal to 0,7. The second scenario uses the prepreg scraps, obtained through the recovery system developed for the Circe project. The quantity of scraps used has been obtained by weighting the effectively used material for production. The quantity of virgin material for the first and third scenarios have been estimated, considering that the final products must have the same mechanical performances in the three scenarios; since the prepreg scraps have lower mechanical properties than the virgin prepreg, the production from scraps will produce a heavier part.

The polyethylene release paper weight percentage has been obtained by weighting a piece of prepreg with and without the release paper. Starting from the percentage weight of the film and the weight of the prepreg needed for the production, the weight of the release paper has been calculated.

The quantity of the consumables used for the compression molding and the autoclave production has been estimated by comparing the present study with previous literature data and by considering the dimension of the sample and catalogues' data.

Table 7. 1 input materials used in the three alternative scenarios

ITEM	MATERIAL	QUANTITY		
		SCENARIO	SCENARIO	SCENARIO 3
Virgin prepreg	prepreg	0,06 kg	-	0,06 kg
Prepreg waste	prepreg	0,028 kg	-	0,028 kg
Prepreg scraps	prepreg	-	0,07 kg	-
Prepreg PE release	Polyethylene (PE)	0,0067 kg	0,0078 kg	0,0067 kg
Release agent	Organic solvent	0,001 kg	0,0012 kg	0,0005 kg
Release paper	Polytetrafluoroethylene	-	-	0,0034 kg
Breather	Polyethylene	-	-	0,01 kg
Vacuum bag	Polyamide 66 (PA66)	-	-	0,035 kg

7.2.2 Prepreg modelling

At present, there is no inventory data for the manufacturing of carbon fibers and prepgs available within the Ecoinvent database. To evaluate the environmental impacts of the production of the prepreg fabric, a model proposed by previous literature studies was used. The impacts related to prepreg production are considered only in the first and in the third scenarios. The production process of prepreg has been detailed in chapter 3. Polyacrylonitrile-based carbon fibers have been considered.

The first phase for the manufacturing of the prepreg is the production of polyacrylonitrile (PAN) fibers through the polymerization of the basic monomer acrylonitrile (AN). The inventory data for this process were taken from the study of Duflou et al (Duflou et al., 2009) and are reported in Table 7.2. Standard high tenacity fibers (1600 g/km) were considered.

Table 7. 2 inventory data for the production of 1 kg of PAN

ITEM	INPUT TYPOLOGY	QUANTITY
input	Acrylonitrile (AN)	1 kg
	Dimethylformamide solvent	0,00335 kg

	Polydimethylsiloxane	0,1 kg
Energy and other resources	Electric energy	60 MJ
	steam	18 Kg

For the modelling of the production of carbon fibers from PAN (considering spinning and stretching, stabilization, carbonization and surface treatment) the inventory data were extracted from the Khalil study (Khalil, 2017). The materials and energy inputs and the outputs are reported in Table 7.3.

Table 7. 3 inventory data for the production of 1 kg of CF

ITEM	ITEM TYPOLOGY	QUANTITY
Input	Polyacrylonitrile (PAN)	1,82 kg
	Air	6,95 kg
	Nitrogen (N ₂)	0,94 kg
Energy and other resources	Thermal energy for PAN fibers oxidation and	0,48 MJ
	Thermal energy for Carbonization of stabilized PAN	7,56 MJ
	Electric energy for CF surface treatment	0,05 MJ
	Electric energy for CF sizing	0,15 MJ
output	Water vapor	0,673 kg
	Carbon dioxide (CO ₂)	0,407 kg
	Hydrogen cyanide (HCN)	0,255 kg
	Carbon monoxide (CO)	0,038 kg
	Nitrous oxide (N ₂ O)	0,0007 kg
	Air	6,07 kg
	Hydrogen (H ₂)	0,00023 kg
	Ammonia (NH ₃)	0,023 kg
	Nitrogen (N ₂)	1,183 kg
	Ethane (C ₂ H ₆)	0,0078 kg
	Ethene (C ₂ H ₄)	0,0073 kg
	Methane (CH ₄)	0,042 kg

The last operation is prepegging, by which the fibers are embedded in an epoxy matrix. The process has been modelled according to literature (Song et al., 2009), considering a prepreg composed of 64% carbon fibers and 36% epoxy resin. Table 7.4 presents the inventory data used in this phase.

Table 7. 4 inventory data for the production of 1 kg of prepreg

ITEM	ITEM TYPOLOGY	QUANTITY
input	Carbon fiber (CF)	0,64 kg
	Epoxy resin	0,36 kg
Energy and other resources	Electric energy	40 MJ

During the production of the prepreg, a layer PE release paper is applied to prevent the adhesion of the prepreg. The weight percentage of the PE paper may vary depending on the type of prepreg used; the value considered in this analysis has been obtained by weighting a piece of prepreg with and without the release paper. A percentage weight of PE equal to 10% of the total weight has been considered.

7.2.3 Equipment used

The different scenarios use different molds and countermolds (if any). All those tools are considered to be made in aluminium. Regarding the CM production with prepreg scraps, the weight of the mold and the countermold has been estimated considering the part and the equipment 3D model.

For the production by CM with virgin prepreg, the weight of the mold and the countermold has been estimated as shown in the equation 7.1:

$$w_1 = w_2 \cdot \frac{P_1}{P_2} \quad (7.1)$$

With:

- w_1 the weight of the mold (or countermold) for the first scenario (kg)
- w_2 the weight of the mold (or countermold) for the second scenario(kg)
- P_1 the estimated weight of the part produced in the first scenario (kg)
- P_2 the measured weight of the part produced in the second scenario (kg)

About the autoclave production, the mold weight has been considered the same as the mold of the first scenario. In the autoclave production, a countermold is not needed.

According to the indication of the involved company, each aluminium mold can be used for producing 750 CFRP parts. The energy consumption associated with the milling of the tools is automatically calculated by the software SimaPro considering the material removed by the milling machine. The weight data for the equipment are reported in Table 7.5.

Table 7. 5 equipment inventory data

EQUIPMENT	ITEM	QUANTITY (kg)		
		SCENARIO 1	SCENARIO 2	SCENARIO 3
Aluminium mold	Input Aluminium	16,66	19,44	16,66
	Aluminium scraps	1,66	1,94	1,66
	Mold final weight	15	17,5	15
Aluminium countermold	Input Aluminium	23,14	27	-
	Aluminium scraps	9,43	11	-
	Countermold final weight	13,71	16	-

7.2.4 Energy consumption

The electrical energy consumption data derive from estimates and literature studies.

To produce the part by CM using prepreg scraps, electrical energy is needed for the milling of the mold and the countermold, the cutting of the prepreg scraps, the peeling of the PE release paper from the scraps, the storage phase and the curing phase. The energy consumptions of the cutting and peeling machines have been calculated considering the rated power of the machines, their productivity, and the weight of the prepreg used. The energy consumption of the refrigerator has been calculated considering the storage time, the volume of the prepreg used, the capacity and the rated power of the refrigerator (the rated power was taken from a technical data sheet of a refrigerator in commerce).

The production by CM with virgin prepreg is very similar to the case above but the cutting of the prepreg scraps phase is substituted by the cutting of the virgin prepreg phase, and the

PE peeling phase is manual, so no electrical energy consumption is associated with it. Moreover, due to the different weight of the raw materials used, the curing phase in this case has lower energy consumption. The energy consumption of the virgin prepreg curing phase has been estimated by considering the energy consumption of the curing phase for the second scenario and the ratio between the weight of the part produced in the second scenario and the estimated weight of the part produced in the first scenario.

The energy consumption for the cutting phase of the first scenario has been estimated on the basis of the part perimeter, the cutting machine speed and the nominal power, according to the following equation.

$$E = W \cdot \frac{P \cdot n}{v_c} \quad (7.2)$$

With:

- E, the energy consumption of the cutting phase (kWh)
- W, the nominal power of the cutting machine (kW)
- P, the part perimeter (m)
- n, the number of templates needed
- v_c , the cutting speed (m/h)

Regarding the third scenario (the autoclave production), the energy consumption of the cutting phase is considered to be the same as the first scenario. The curing phase energy consumption has been estimated on the basis of the study of Song et al (Song et al., 2009). The lay-up phase is considered completely manual for all the three scenarios. Table 6.6 shows the results of the inventory phase for the energy consumption.

Table 7. 6 energy consumption in the three scenarios

MANUFACTURING PHASE	QUANTITY		
	SCENARIO 1	SCENARIO 2	SCENARIO 3
Cutting virgin prepreg	0,01 kWh		0,01 kWh
Cutting prepreg scraps	-	0,0004 kWh	-
Peeling prepreg scraps	-	0,0065 kWh	-
Lay-up phase	-	-	-

Curing autoclave	-	-	0,37 kWh
Curing compression molding	1 kWh	1,2 kWh	-
Storage energy consumption	0,082 kWh	0,0672 kWh	0,082 kWh

7.2.4 Transportation

Most of the transport data for this analysis have been taken from a literature study of Forcellese et al that involved the same company of this analysis. The data of the previous article were estimated on the basis of indication provided by key managers of the company and considering average distances among supplier and customer sites. The geographical locations of the companies involved in the production chain are reported as follow:

- Carbon fiber producer: Japan
- Epoxy resin producer: Germany
- Prepreg producer: Central Italy
- Aluminium producer: Germany
- Aluminium mold producer: Central Italy
- CFRP part producer: Central Italy

Table 7.7 shows the inventory data related to transports. For the weight of the materials used see the previous tables of this chapter.

Table 7.7 inventory data related to transportation

TRANSPORTATION	DISTANCE (km)	TRANSPORTATION TYPOLOGY
Carbon fibers	150	Truck 16-32 ton
	16800	Transoceanic ship
Epoxy resin	1200	Truck 16-32 ton
Virgin prepreg	30	Truck 3,5-7,5 ton
Raw Aluminium	1200	Truck 16-32 ton
Aluminium molds and countermolds	12	Truck 3,5-7,5 ton
Aluminium waste	200	Truck 16-32 ton

7.3 Life cycle impact assessment

To guarantee a complete view of the environmental impacts associated with the three scenarios of this study, the following impact categories have been considered:

- Cumulative energy demand (CED).
- Global warming potential (GWP).
- Midpoint and endpoint of the ReCiPe methodology.

All of those indicators have been widely used in literature LCA studies to evaluate the environmental impacts of CFRP products. Some relevant literature studies which used those indicators are listed below:

- CED: Das, 2011; Duflou et al., 2012; Raugei et al., 2015;
- GWP: Das, 2011; Duflou et al., 2012; Khalil, 2017; Raugei et al., 2015; Umair, 2006; Robert A. Witik et al., 2011; Witik et al., 2013, 2012
- ReCiPe: Duflou et al., 2012; Khalil, 2017; Raugei et al., 2015; Umair, 2006; Robert A. Witik et al., 2011; Witik et al., 2013, 2012

7.4 Results and Discussion

In this section, the results of the Life Cycle Impact assessment calculated by using the inventory data in different environmental impact categories are shown.

7.4.1 Cumulative Energy Demand

Figures 7.3 and 7.4 illustrate the results of the environmental evaluation of the three production systems in terms of CED. The second scenario (compression molding with recycled prepreg) presents the lowest environmental load (27,7 MJ) whilst the first scenario is associated with the highest impacts (76,2 MJ). The CED result for the total impact of the third scenario is 69,8 MJ. By estimating a linear trend of environmental savings of the second scenario with the weight of products made, the CED saved per kg of recycled CFRP waste would be 601,5 MJ.

The main contribution for the scenarios 1 and 3 is attributable to the raw material used; as reported in previous studies, the production of carbon fibers/epoxy resin prepgs, due to

the energy required for the carbon fibers production, has a great environmental impact. In this study, the impacts related to the prepreg represent about 70% of the total impacts (69% for the first scenario and 75% for the second scenario). A previous study carried out by Forcellese et al showed that, for the production of CFRP parts with a weight of 15,7 kg and with production processes similar to those considered in the present study, the contributions of the prepreg used accounted more than 90% of the impacts. Since by mean of the recycling process virgin prepreg is saved, as the contribution on the total impacts of the raw material used increases, the environmental savings related to the recycling of the prepreg scraps are expected to increase. That would be the case of industrial applications of the prepreg recovery process.

The tooling phase, which includes the impacts of the raw aluminium used for the molds, the transport of both the raw material and the finished molds, and the energy consumption of the milling machine, has different impacts for the three scenarios. The total impact associated with the production of the aluminium tools has been divided by the number of parts that they can produce. It accounts 14,07 MJ in the first scenario and 16,4 MJ in the second scenario. The difference in the tooling contribution between the first two scenarios is imputable to the higher weight of the aluminium tools in the second scenario. Scenario 3 has the lowest impact for the tooling phase (5,3 MJ) because the aluminium mold is the only tool needed whilst in the other two production processes a countermold is needed too.

For what concerns the curing phase, the highest energy consumption is associated with the second scenario as more thermal energy is required to cure heavier products (with heavier molds). In line with other previous studies results, the impact associated with the curing phase of the autoclave scenario is lower than the impact of the curing phase of the compression molding scenarios. This behaviour can be attributable to the higher mass of tools used in the compression molding processes. The storage phase has the same impacts for scenarios 1 and 3 while the CED is about 20% lower for the second scenario. In fact, all the material stored for the second scenario is used in the compression molding process while for the virgin productions, 30% of the stored material becomes a waste after the cutting phase (the nesting efficiency is considered to be 70%).

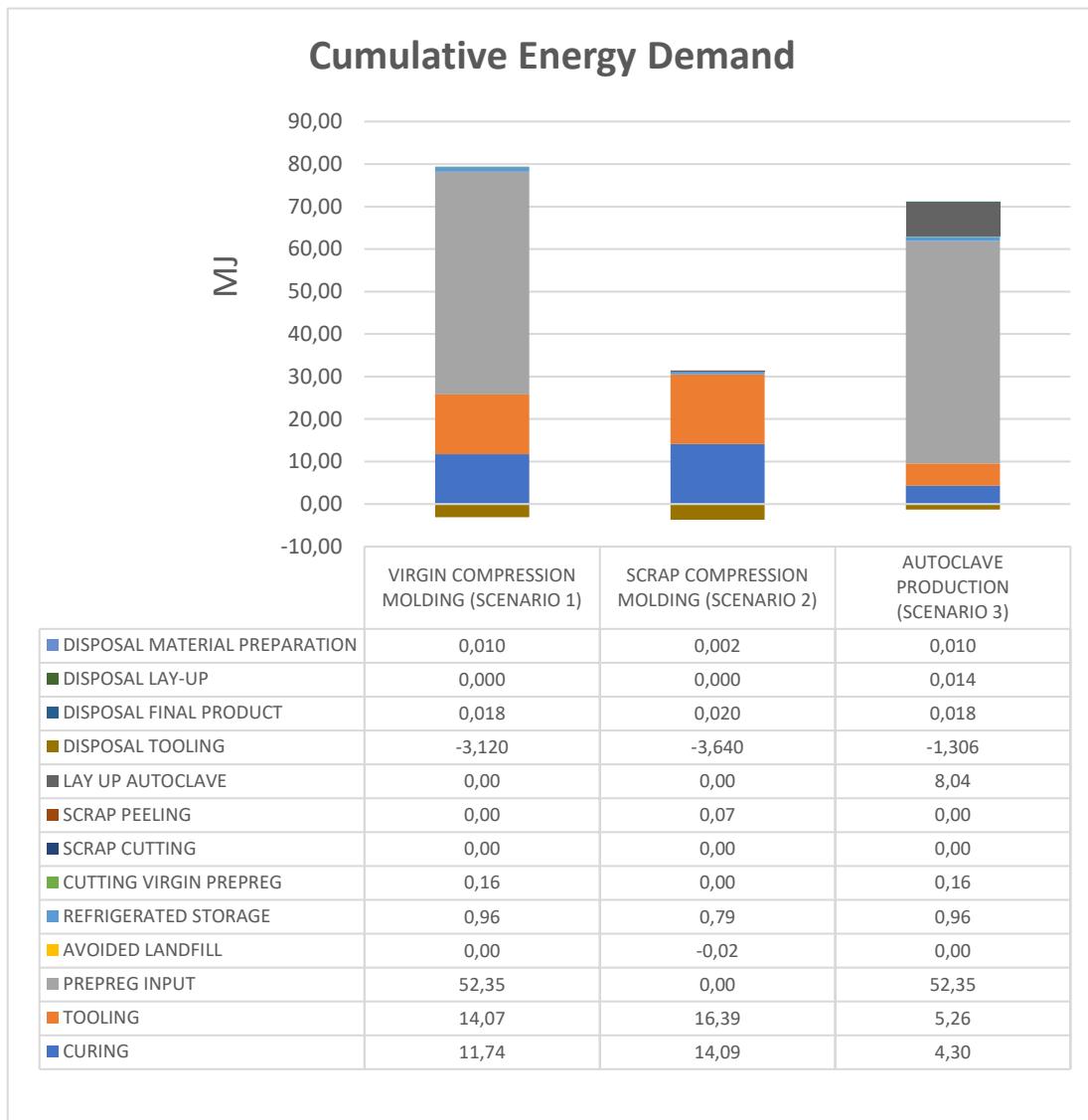


Figure 7. 3 Cumulative Energy Demand for the three scenarios

The impact associated with the waste recovery process is negligible. By comparing it with the environmental savings obtained from the recycling of the PE film peeled from waste, the graph shown in Figure 7.5 is obtained. It emerges that the energy saving associated with the recycling of the release paper exceeds the consumption of the preparation stage. However, the main advantage of the recycling process is given by the reuse of the material and the saving of virgin material.

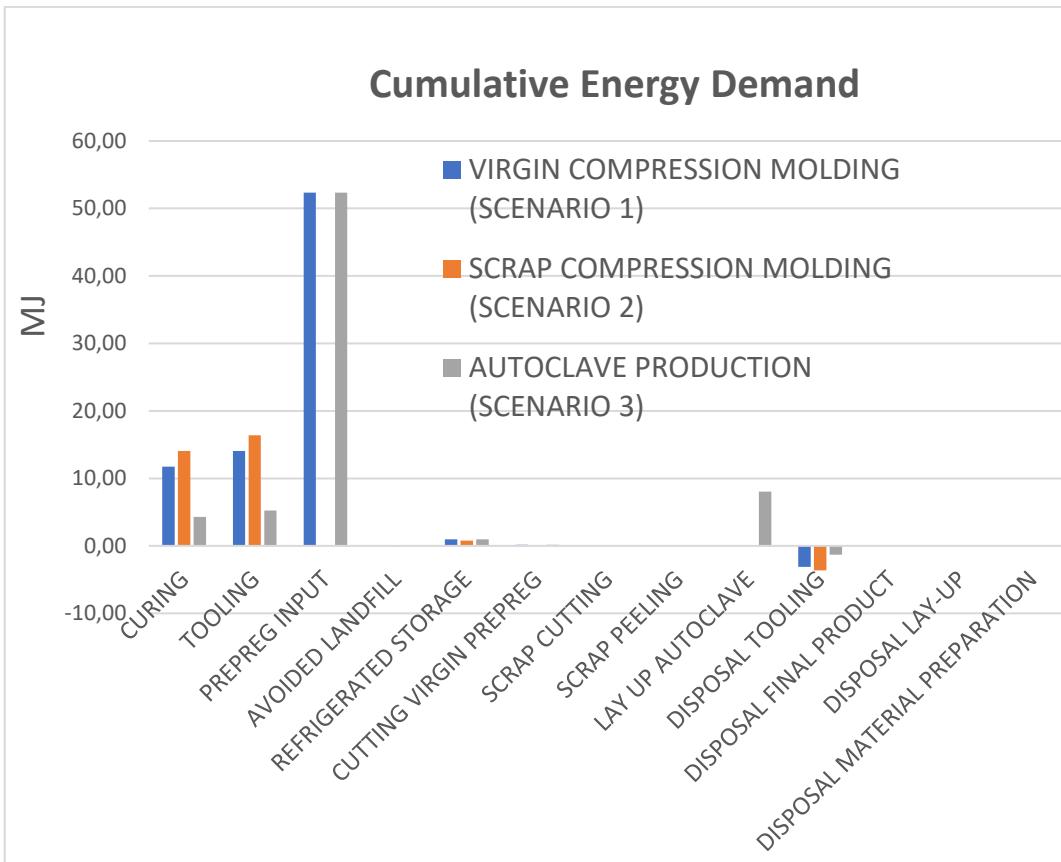


Figure 7. 4 CED values for all the phases considered in the three scenarios

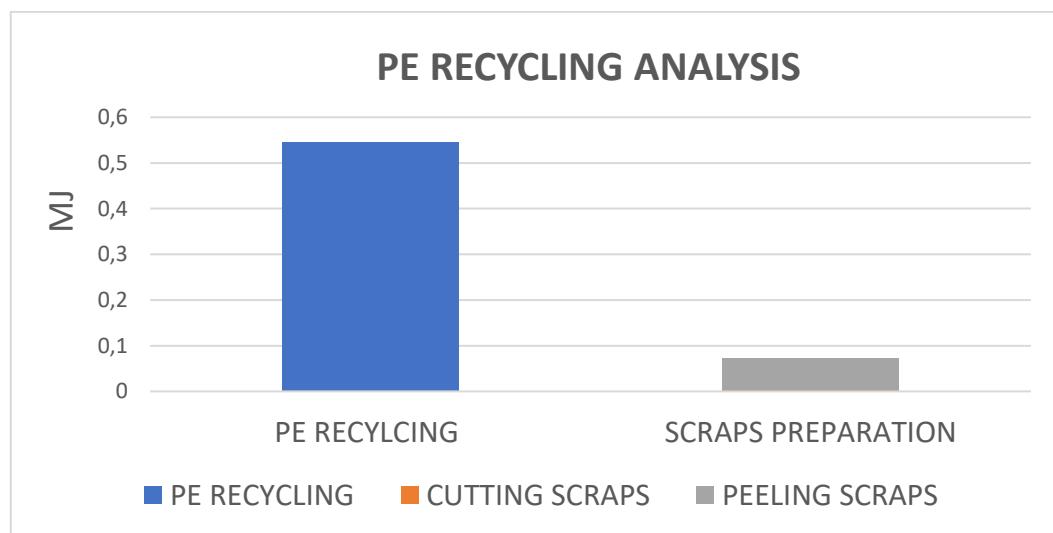


Figure 7. 5 Cumulative Energy Demand analysis of the PE release paper recycling

Image 7.6 shows the CED values as a function of the production volume. For low production volumes, autoclave production has the lowest environmental impact. This is due to the lower weight of the tool used in that scenario (no counter-mold is needed). Excluding the tooling phase, the second scenario has the lowest environmental load. Therefore, as the production volume increases, two break-even points are reached (at 27 and 129 products), and the production with recycled material became the best environmental alternative.

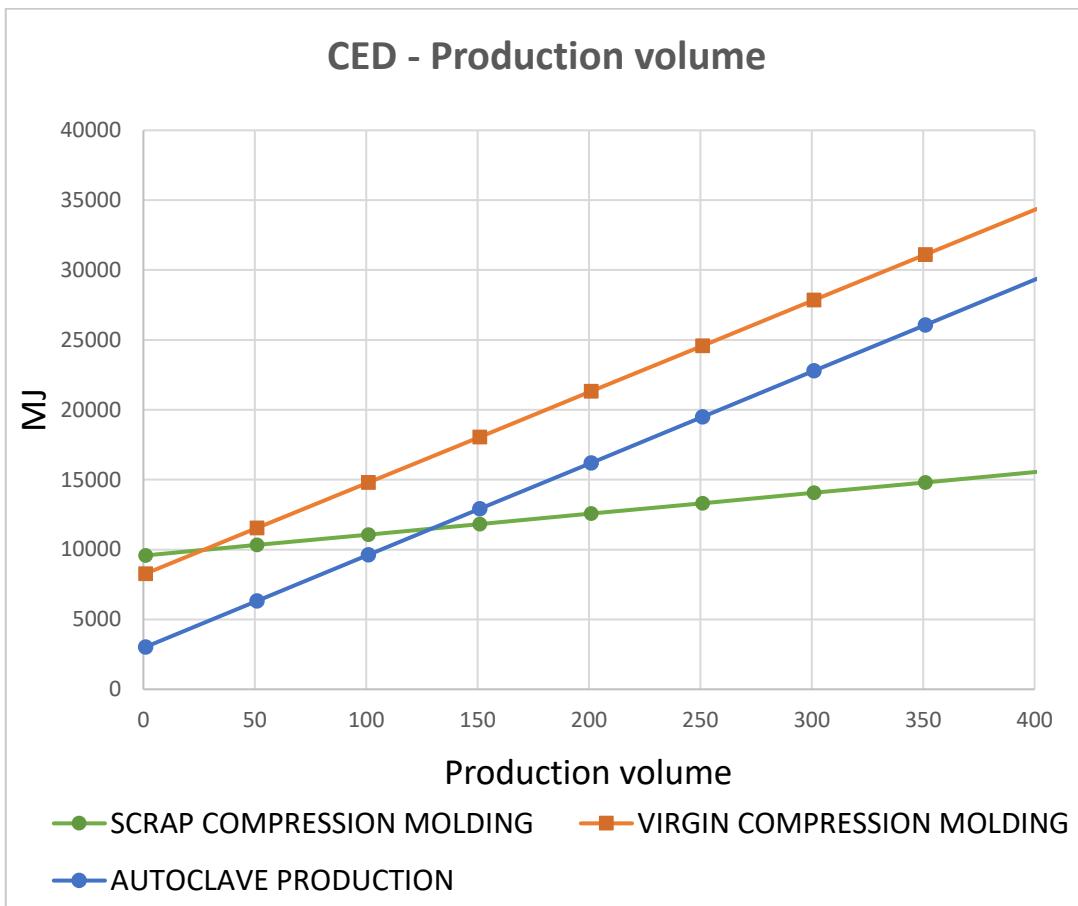


Figure 7. 6 CED – production volume results

7.4.2 Global Warming Potential (GWP)

The results calculated for the Global Warming Potential (GWP) are presented figures 7.7 and 7.8. The second scenario has, once again, the best environmental performance; it has a GWP value of 2,1 kg eq CO₂, which is less than half the values of GWP of the other two alternatives. Regarding the other two scenarios, differently from CED results, using the GWP indicators the autoclave production has the highest environmental load. The main difference between the CED and GWP results is represented by the percentage contribution of the lay-up phase for the autoclave production. Using the CED indicator, the lay-up accounts around 10% of the total impacts, while, considering the GWP, it accounts for almost 30% of the environmental load. The main contribution of the lay-up phase is attributed to the PTFE (polytetrafluoroethylene) release film. Even if the film used has a low mass (0,0034 kg), it causes a high contribution due to the very high unitary GWP of the PFE (303 kg eq CO₂ per kg of PTFE).

The recycling scenario leads to a saving of 37,4 kg eq CO₂ per kg of CFRP recovered. To complete the analysis, it is useful to compare the environmental benefits of the CIRCE recovery system with other recycling systems. Comparing the saving of this study with previous literature analysis, the uncured prepreg recovery process seems to have more environmental benefits than the traditional recycling processes. For example, Meng et al (Meng, Pickering, et al., 2018) analysed the environmental performance of different recycling procedures for CFRP waste. In that case, it was assumed that the waste was composed by 55%wt fibers and 45%wt matrix. It emerged that the fluidised bed recycling process was the best alternatives and it provided a saving of 25,9 kg eq CO₂/kg of CFRP recovered. The saving associated with other EoL options, like landfill, incinerator, pyrolysis, and mechanical recycling was lower. So, considering the Meng et al study, the CIRCE recycling process provides an eq CO₂ saving that is at least 44% higher than the other available recycling processes.

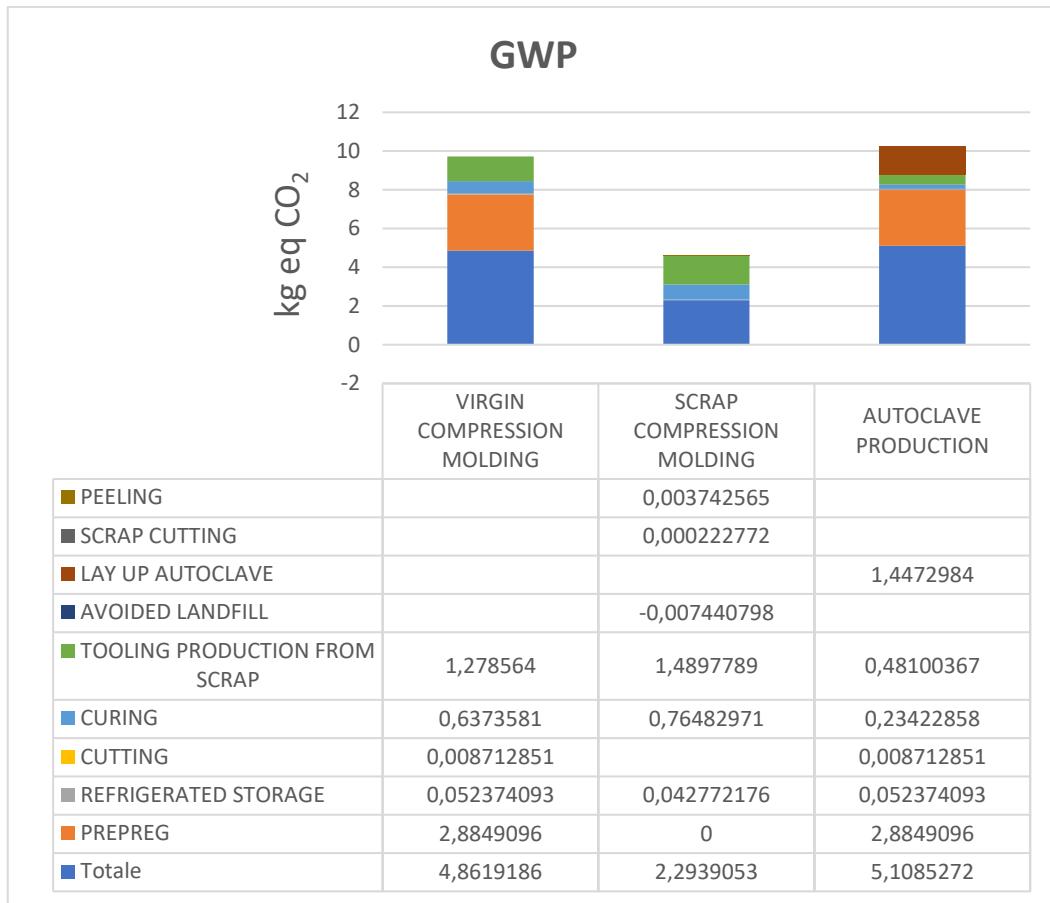


Figure 7. 7 LCIA results in terms of GWP

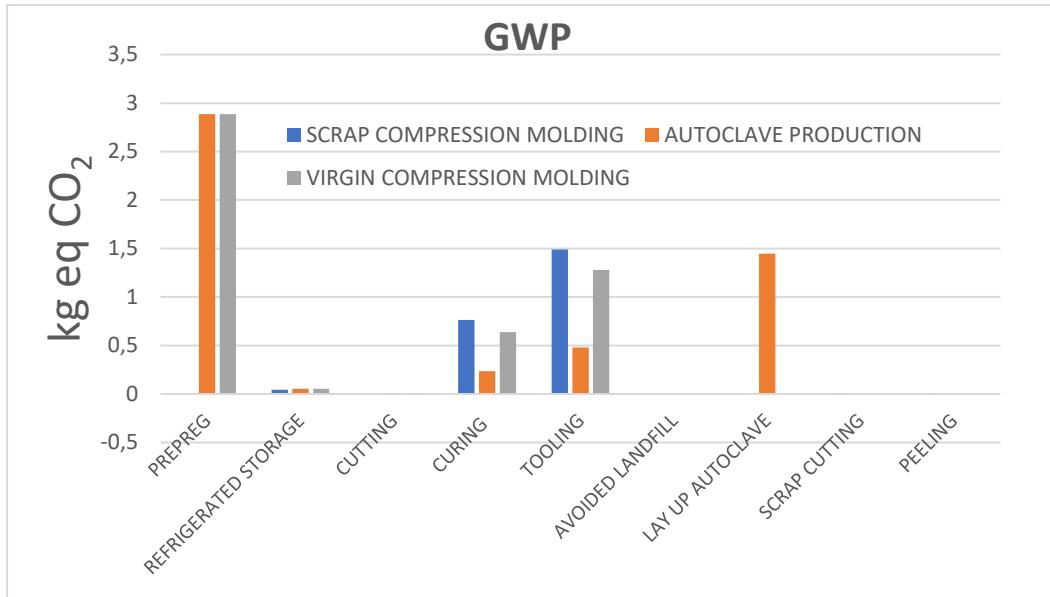


Figure 7. 8 LCIA results in term of GWP for each production phase

7.4.3 ReCiPe

The results of the ReCiPe midpoint level are reported in Table 7.8. and in Figures 7.9 and 7.10.

Table 7. 8 ReCiPe midpoint results

Impact category	Unit of	Virgin	Scrap	Autoclave
Climate change	kg CO ₂ eq	4,63E+00	2,05E+00	5,07E+00
Ozone depletion	kg CFC-11 eq	4,28E-07	1,14E-07	3,24E-05
Terrestrial	kg SO ₂ eq	2,86E-02	1,32E-02	2,36E-02
Freshwater	kg P eq	1,03E-03	5,13E-04	8,36E-04
Marine	kg N eq	1,16E-02	4,26E-03	1,04E-02
Human toxicity	kg 1,4-DB eq	2,66E+00	5,78E-01	2,50E+00
Photochemical	kg NMVOC	1,54E-02	6,64E-03	1,31E-02
Particulate matter	kg PM10 eq	9,36E-03	4,55E-03	7,59E-03
Terrestrial	kg 1,4-DB eq	4,59E-02	6,50E-05	4,59E-02
Freshwater	kg 1,4-DB eq	7,68E-02	3,87E-02	6,12E-02
Marine ecotoxicity	kg 1,4-DB eq	7,64E-01	3,51E-02	7,50E-01
Ionising radiation	kBq U235 eq	4,54E-01	1,55E-01	4,09E-01
Agricultural land	m ² a	1,47E-01	2,16E-02	1,51E-01
Urban land	m ² a	2,54E-02	1,51E-02	1,87E-02
Natural land	m ²	6,11E-04	2,66E-04	4,92E-04
Water depletion	m ³	4,58E-02	1,27E-02	4,98E-02
Metal depletion	kg Fe eq	6,94E-02	2,33E-02	6,38E-02
Fossil depletion	kg oil eq	1,42E+00	4,96E-01	1,30E+00

Since the impact categories have a different unit of measure, the data were processed to create graphs easy to understand. In figure 7.8, each value is divided by the maximum value obtained for its impact category. In general, the results are in line with the results obtained for the CED indicator. The second scenario has the lowest environmental load for every midpoint category. For most of the impact categories, the first scenario has the worst behaviour. In the case of Climate change, Ozone depletion, Agricultural land occupation and

Terrestrial ecotoxicity, the autoclave production has the highest impacts. This is due to the tetrafluoroethylene used in the release paper for the lay-up phase.

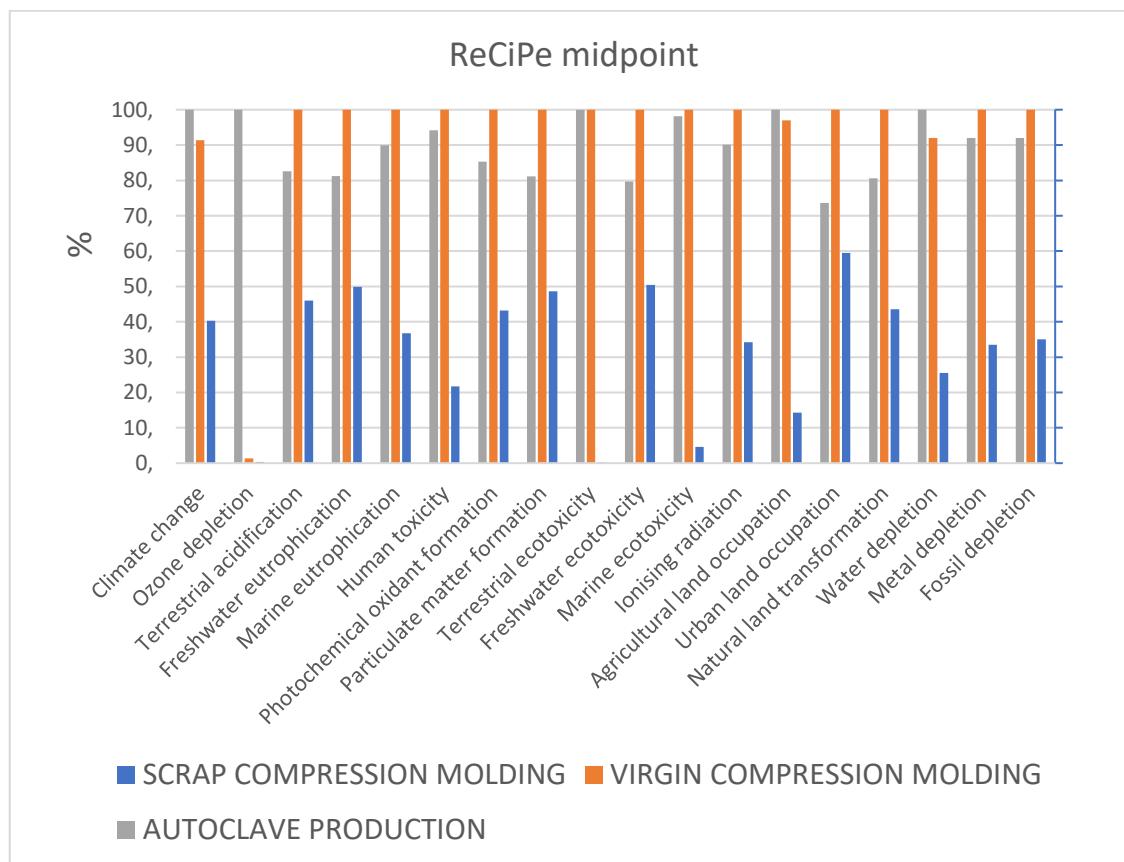
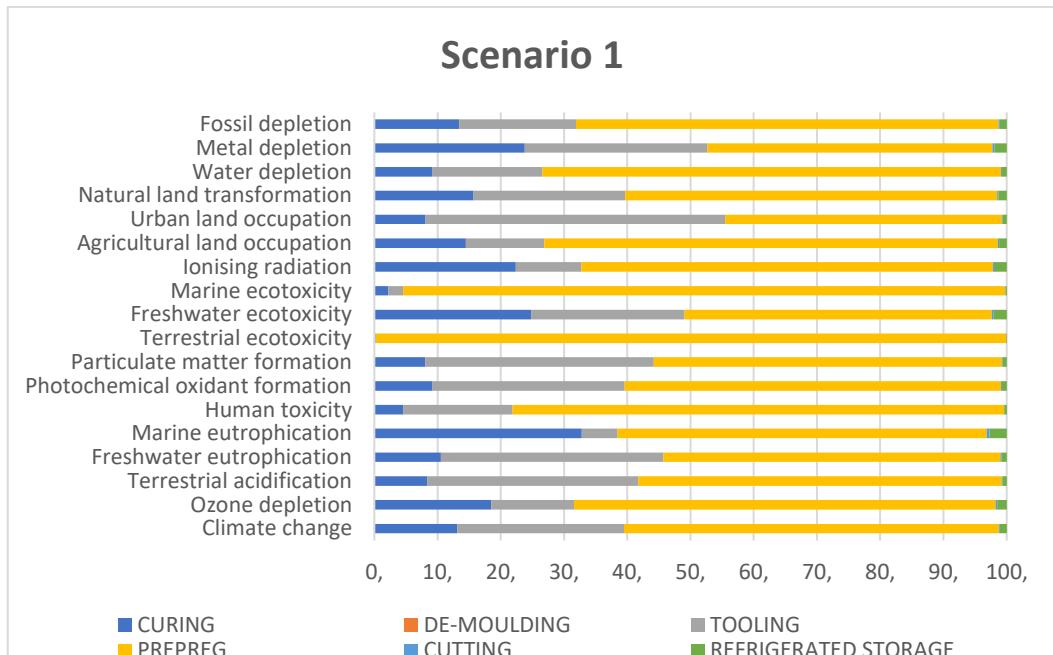
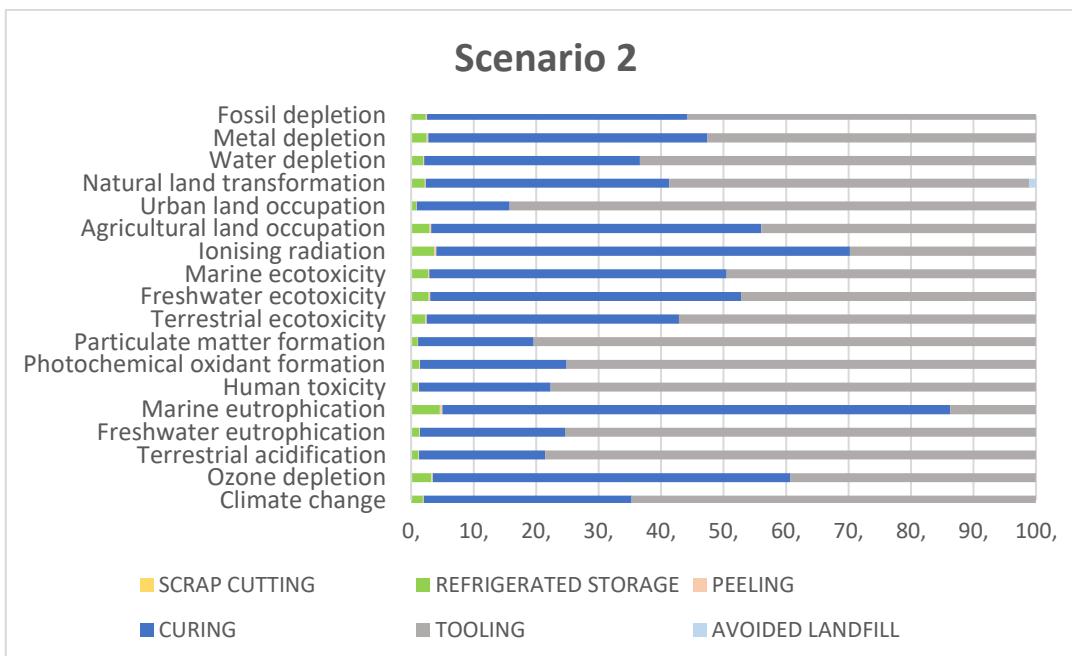


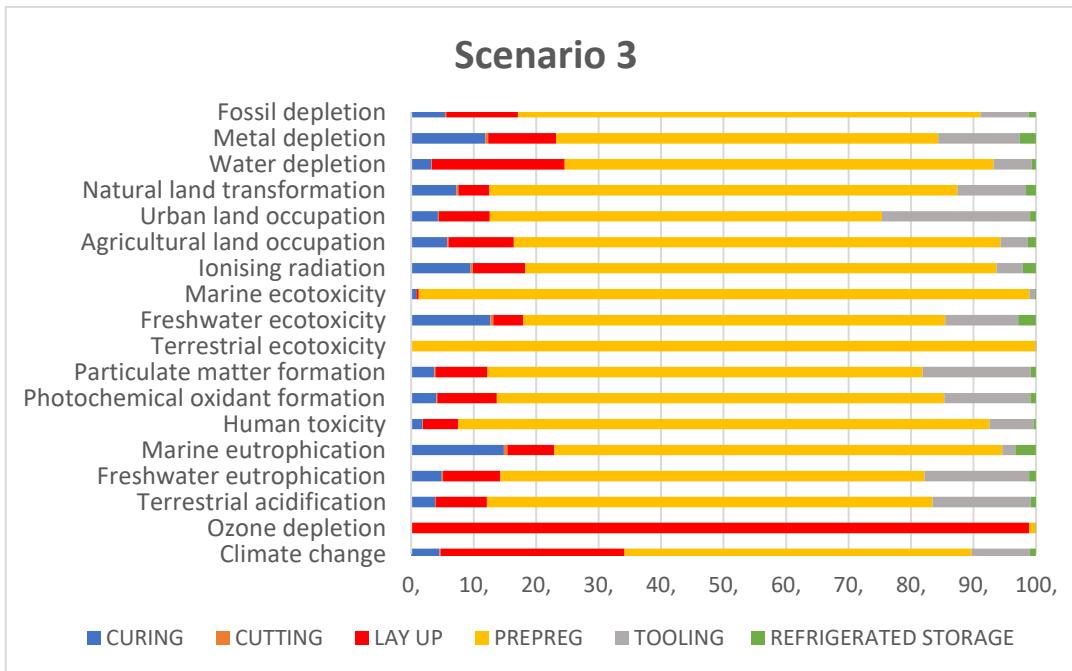
Figure 7. 9 comparison of the three considered scenarios



a)



b)



c)

Figure 7. 10 percentage contribution of each input in the three scenarios:

a) scenario 1, b) scenario 2, c) scenario 3

The impacts of the midpoint categories are mainly determined by three inputs: the energy consumption of the curing phase, the prepreg used and the production of the molds. In the first and third scenario, the material used has the most important impact in almost all categories. The preparation process for the uncured scraps has negligible impacts for all the midpoints. For autoclave production, the use of consumables in the lay-up phase has an important contribution for several indicators. The tetrafluoroethylene used for the release paper determines almost all impacts for the Ozone depletion indicator.

Lastly, an endpoint analysis has been carried out to have a single score also in terms of the ReCiPe method. Figure 7.11 confirms the trend found considering CED and GWP indicators.

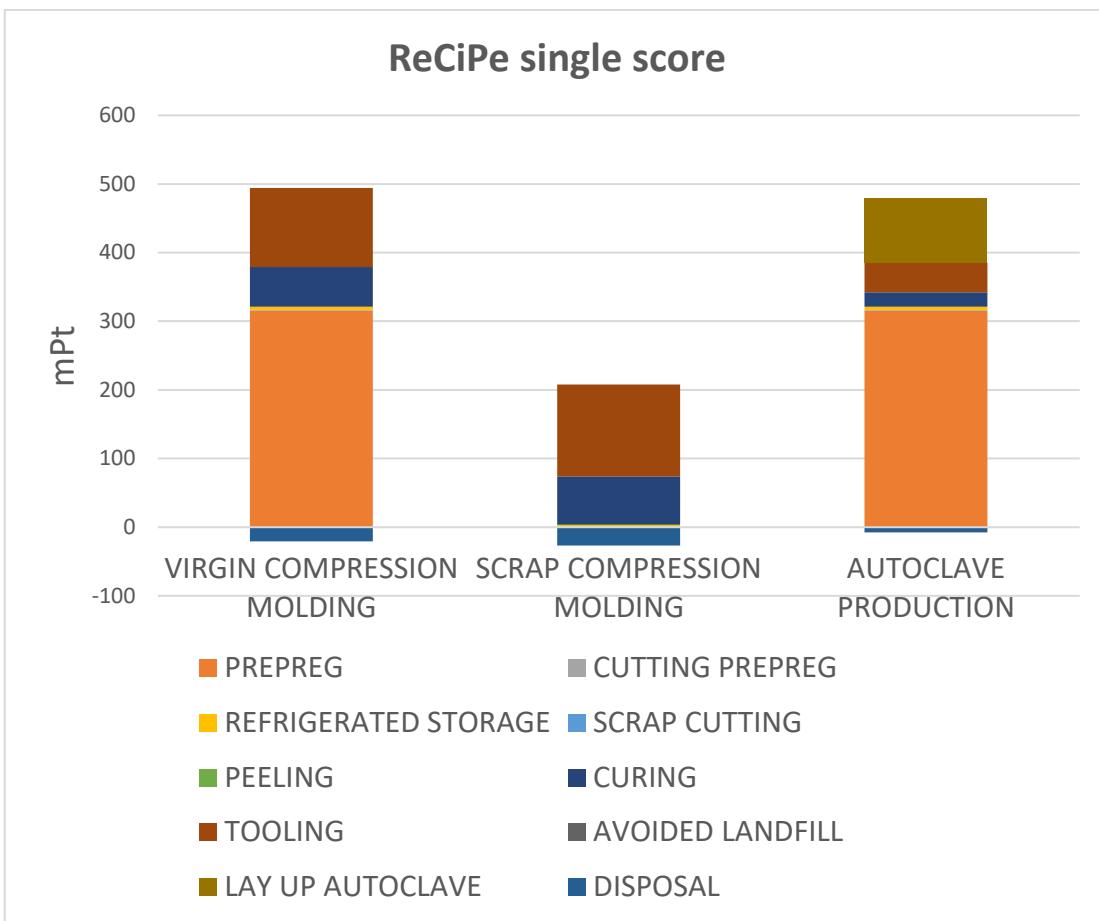


Figure 7. 11 ReCiPe single score results

7.5 Life Cycle Cost (LCC)

A cost estimation analysis has been carried out to compare the three scenarios and to evaluate the economic feasibility of the recovery process. A parametric approach was used in the study. Using this method, the cost of a product is evaluated using parameters which have been identified as the cost drivers. The parameters may concern, for example, physical characteristics, such as mass and volume, the number of input-outputs, labour, and energy. Starting from the parameters, the total cost can be estimated using three different parametric methods:

- the method of the scales uses analogies with other products considering linear relationships between the value of the considered parameter and the cost.
- the statistical model uses a set of statistical relationships which are considered to be universal.
- The cost Estimation Formula (CEF) method uses simple mathematical relationships to connect the cost of a product or an activity to technical parameters.

The production process is segmented into unitary activities and the total cost is calculated as the sum of costs of each unitary activity. The cost of the tools or the machines is calculated considering the production volume.

It is a simple and fast method but there are some issues associated with it. The cost estimation formulas (CEFs) may need some values that are not always available, so the model will need some of the parameters to be estimated. This will cause uncertainty in the results. In some cases, the CEFs may not consider important parameters leading to considerable errors in the cost's evaluation (Duverlie & Castelain, 1999).

The Life Cycle Cost analysis carried out in this study considers the same functional unit and the same scenarios of the previous LCA analysis. Data about the quantity of energy and materials are the same used for the LCA analysis. In the cost model, all the direct costs and the machine deprecations are considered. The depreciation cost is considered because two new machines were specifically developed for the CIRCE project and their cost must be taken into account to evaluate the economic convenience of the recovery process.

As in the case of the impact analysis, the data used comes from several sources:

- Most of the data was provided by the company involved. The costs of consumables and virgin prepreg, the costs of the machines used and their useful life, the hourly cost of labour, the cost of electricity, the nominal power of some of the machines used, the cost of the molds of the second scenario, and the cost for the disposal of production waste are part of this data category.
- Some data have been hypothesized on the basis of the information provided by the company and previous data from the scientific literature. Some examples are the energy consumption of the press and autoclave, and the labour time.
- Part of the data has been calculated on the basis of the previous information and the Life Cycle Inventory analysis (i.e. the depreciation costs of the machines used).

The following table summarizes the cost inventory data for all the three scenarios.

Table 7. 9 LCC data

	COST	Cost for product		
PREPREG	80 €/kg	5,33 €	0,00 €	5,33 €
PREPREG WASTE	0,65 €/kg	0,02 €	0,00 €	0,02 €
PE WASTE DISPOSAL	0,27 €/kg	0,00 €	0,00 €	0,00 €
RELEASE AGENT	20 €/kg	0,02 €	0,02 €	0,01 €
VACUUM BAG	1,4 €/kg			0,05 €
BREATHER	25 €/kg			0,25 €
RELEASE PAPER	34,5 €/kg			0,01 €
LABOUR	20 €/h	20,00 €	22,00 €	30,00 €
MOLD CM VIRGIN	475 €	0,63 €	0,00 €	
COUNTERMOLD CM VIRGIN	475 €	0,63 €	0,00 €	
MOLD SCRAP CM	570 €		0,76 €	
COUNTERMOLD SCRAP CM	570 €		0,76 €	
MOLD AUTOCLAVE	475 €			0,63 €
PRESS	15000 €	0,32 €	0,32 €	
REFRIGERATOR	600 €	0,00 €	0,00 €	0,00 €
CUTTING MACHINE	180000 €	0,00 €	0,00 €	0,00 €

AUTOCLAVE	220000 €		0,00 €	0,25 €
CUTTING SCRAP MACHINE	20000 €		0,00 €	
PEELING MACHINE	6000 €		0,00 €	
PRESS ENERGY CONSUMPTION	0,17 €/kWh	0,17 €	0,20 €	
STORAGE ENERGY CONSUMPTION	0,17 €/kWh	0,01 €	0,01 €	0,01 €
CUTTING ENERGY CONSUMPTION	0,17 €/kWh	0,00 €	0,00 €	0,00 €
AUTOCLAVE ENERGY CONSUMPTION	0,17 €/kWh			0,06 €
CUTTING SCRAP ENERGY CONSUMPTION	0,17 €/kWh		0,00 €	
PEELING ENERGY CONSUMPTION	0,17 €/kWh		0,00 €	
TOTAL		27,15 €	24,09 €	36,64 €

For each scenario, the total cost associated to every material has been calculated by multiplying the cost per kg of the material by the quantity used in that scenario. The mold cost for the second scenario was part of the involved company set of data. The molds cost for the first and third scenario was estimated by considering the cost of the tools for the second scenario and the weight ratio of the parts to be realized in the two scenarios. The costs of the molds have been divided by the number of parts they can produce during their useful life.

The depreciation costs of the machines used have been calculated by considering their purchase price, their capacity, their estimated useful life, the time of use of the machines per production cycle, and data about the materials used (weight, and volume). Except for the press and the autoclave, the depreciation cost of the machines is negligible. This depends on the fact that the machines have a much longer useful life than the analysed production run. Even for the case of the press and the autoclave, their contributions on the cost is not of large importance. The low voltage energy cost was considered 0,17 €/kWh.

The labour cost has been calculated by multiplying the labour hourly cost by the estimated time of labour. The labour time was estimated on the basis of a previous literature LCC study. The autoclave production requires more labour time than compression molding productions

because of a more time-consuming manual layup. Therefore, the third scenario is associated with the highest labour cost. The second scenario has a higher labour cost in comparison with the first one because of the different weight of the molded parts. The production with recycled material is the most economically viable even though the costs of the tools and the manpower are higher in comparison with the first scenario costs. The cost saving is completely due to the replacement of a high-cost virgin material with a zero-cost recycled material. Autoclave production is the most expensive of the three alternatives because of the high labour costs.

Figures 7.12 and 7.13 show the total costs and the cost contributions of the three scenarios as the production volume changes.

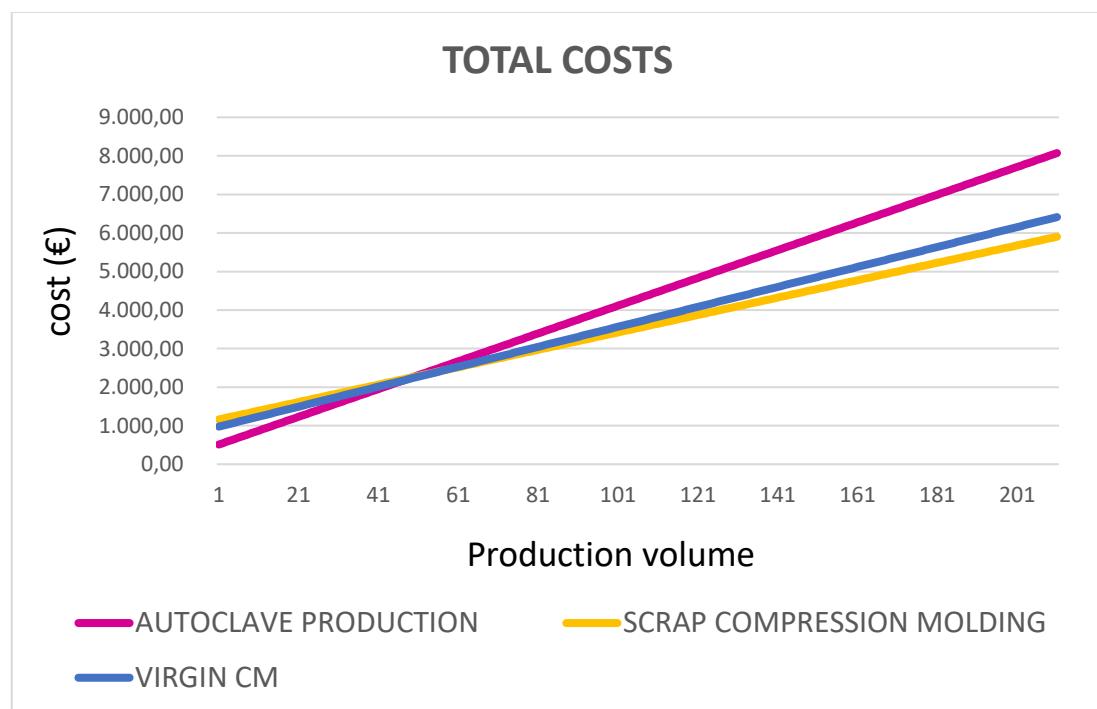


Figure 7. 12 total costs vs production volume for the different production processes

For low production rates, the third scenario is the most economically convenient. In fact, since for the autoclave production a counter-mold is not needed, the total cost of the aluminium tools is lower than the other two alternatives. As the production volume increases, since the cost per unit is the highest for the autoclave production, two break-even points are reached. For a production volume of 49 units, the total cost of the autoclave production reaches the total cost of the second scenario. The break-even point between the first and third scenario is reached for a production volume of 57 units.

As shown in Figure 7.13, for low production rates, the contribution of molds cost is predominant and autoclave production is the most convenient. As the number of parts made increases, the contribution of labour, materials used and energy increases and compression molding productions become the least expensive. Due to the high costs of the molds, for low production volumes the production with recycled material is the most expensive alternative. As the contribution of the material used increases, the saving associated with the reuse of uncured prepreg makes the second scenario the less expensive process.

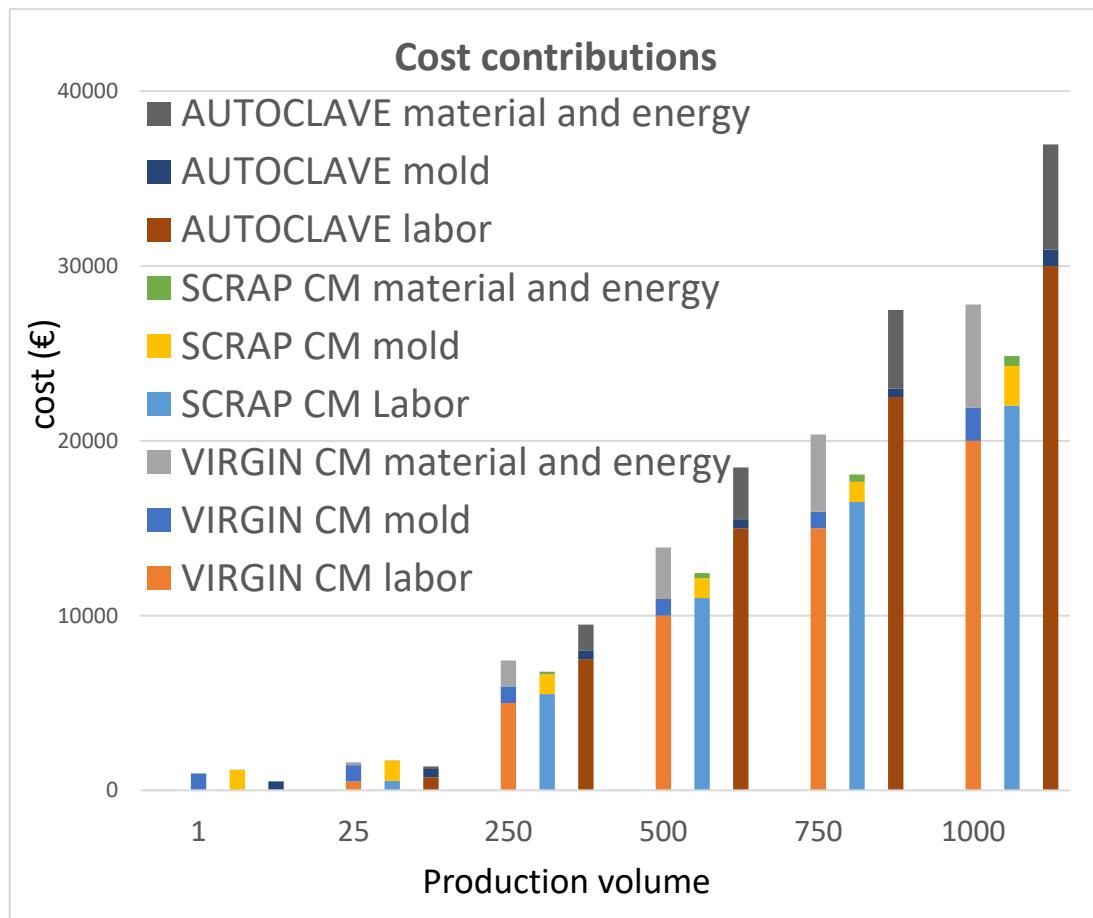


Figure 7. 13 cost breakdown for the three scenarios

The functional unit of this study is a sample of relatively low weight whilst the involved company plans to produce automotive components which have a considerably higher weight than the analysed part. To conclude the study, the variation of the total costs of the production systems in relation to the weight of the realized product was studied. The results

are reported in Figure 7.14. Since the cost saving of the second scenario is related to the saving on the costs of virgin material, as the weight of the products increases, the expected saving increases too.

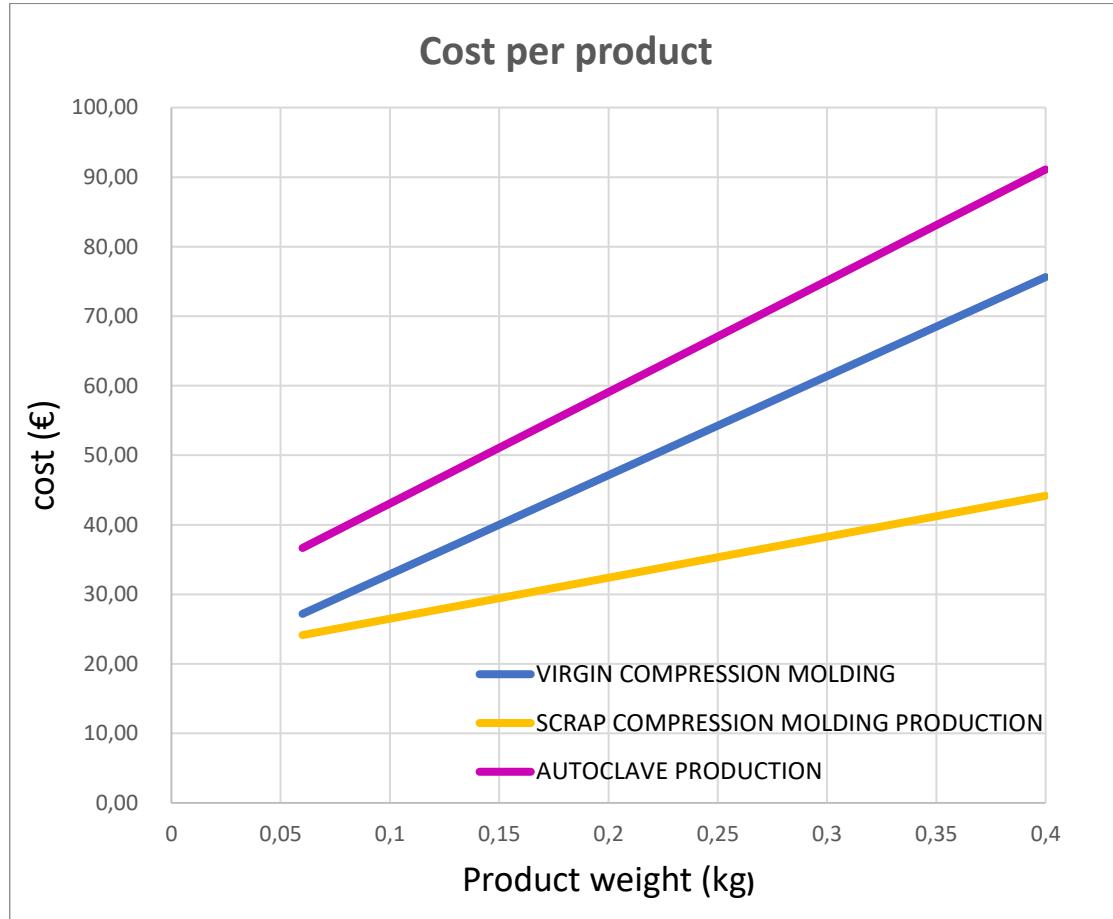


Figure 7.14 total costs vs product weight

CHAPTER 8

LCA ANALYSIS OF THE TOE CAPS PRODUCTION

The second LCA analysis conducted in this study deals with the production of toe caps, used by Base Protection to produce work footwear. The same procedure applied for the HP composites LCA analysis has been followed. At present, the toe caps are made of a thermoplastic polymer-based compound by mean of an injection molding process. CETMA, in collaboration with Base Protection, is evaluating the technical feasibility of the use of the recovered prepreg scraps to produce the toe caps by mean of a CM process.

8.1 Goal of the study and functional unit

The goal of this analysis is to quantify and compare the environmental performances of two different processes (injection molding with virgin material and compression molding with prepreg scraps) for the production of a toe cap used in work footwear. Moreover, a LCC analysis is associated with the LCA analysis to evaluate the economic performances of the two solutions.

The functional unit has been defined as the manufacturing of one toe cap used in the production of a size 8 (US) work shoe. The weight of the part produced by injection molding is 0,077 kg. It has been considered that the CM process would lead to a product of the same weight.



Figure 8. 1 work shoe and cap toe.

Two scenarios have been considered in the comparative analysis to represent the realistic cases:

- Scenario 1
Injection molding production using a thermoplastic-based compound.
- Scenario 2
Compression molding production using recovered prepreg scraps.

8.1.1 System boundaries and scenario description

The LCA carried out for the toe caps production can be classified as a “cradle to gate” analysis. It considers all the impacts related to the extraction of the raw materials, the materials manufacturing and preparation phases, the materials transport, the production phases, and the disposal of the materials used during the production processes. The use phase and the disposal of the toe caps have not been taken into account as the impact related to these phases were considered the same for the two scenarios. The two scenarios are described as follows:

- SCENARIO 1. Injection molding production.
The first scenario deals with the production of the toe caps through an IM process. The material used in the process is a granulated compound composed mainly by polycarbonate. Further details about the composition of the raw material cannot be reported due to confidentiality reasons. After the production and the transport of the thermoplastic compound, the raw material is kept in a dryer for 3-8 hours to remove the moisture from the pellets. The dryer filters are replaced every month with new ones. After the drying phase, the pellets are used to produce the part using an injection molding machine. The molds used in the process are made of steel. The machine produces four parts for every injection cycle.
- SCENARIO 2. Compression molding production with recovered scraps.
The second scenario deals with the production of the functional unit by compression molding using the recovered prepreg scraps. This production process is practically the same as the one described in scenario two of the previous LCA analysis (see chapter seven). The prepreg scraps are cut and peeled by HP Composites, in central Italy. They are then transported to Base Protection, in southern Italy. After a refrigerated storage period, the scraps are used in a CM process. A two cavities aluminium mold is coated with a release agent before its use.

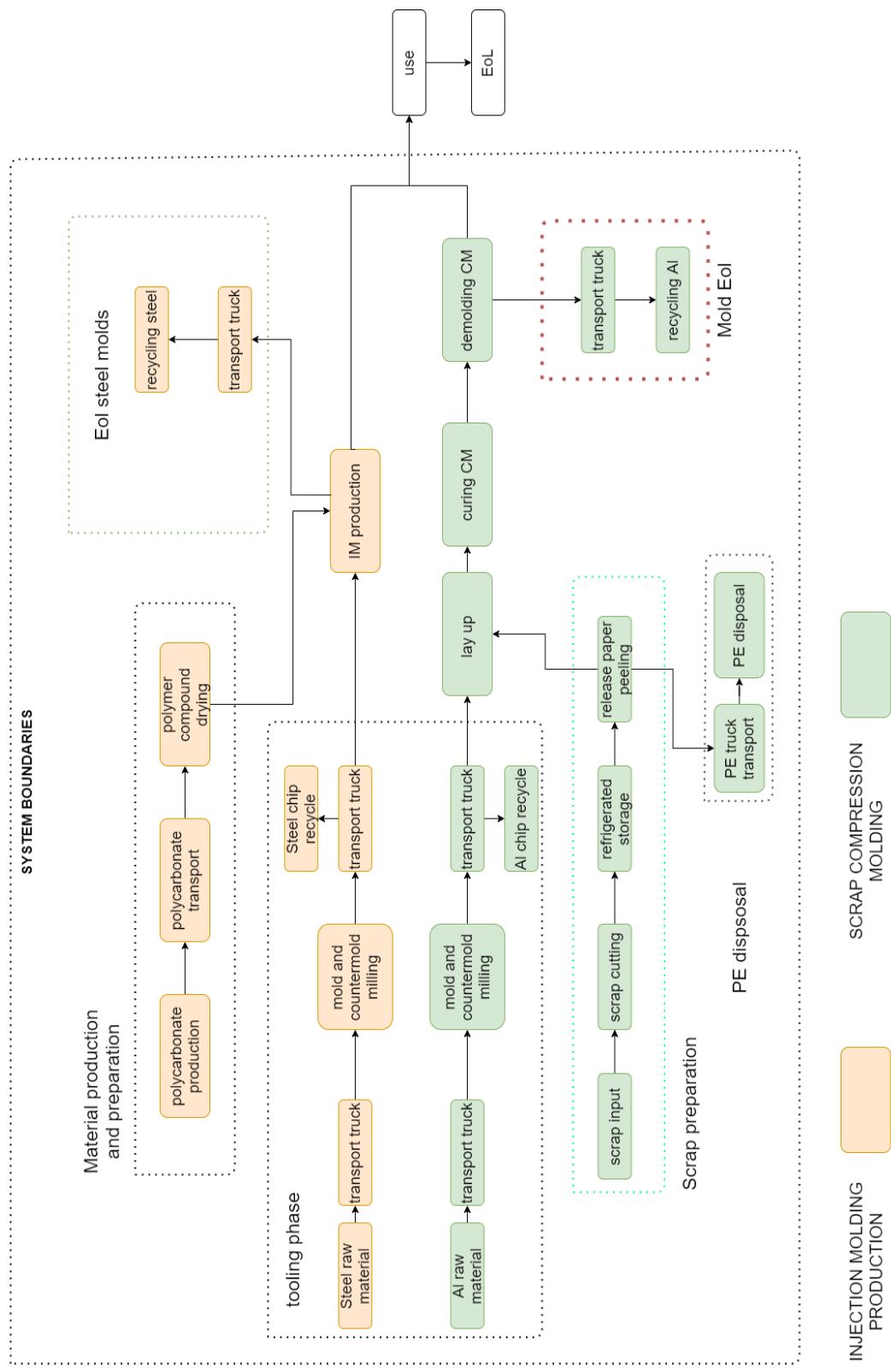


Figure 8. 2 LCA scenarios

8.2 Life Cycle Inventory

This LCI considers all the inputs and outputs of the process within the system boundaries which have relevant environmental impacts. The inventory data were collected from different sources. Primary data were collected by the involved companies. Secondary data were taken from literature research and the Ecoinvent 3.1 database.

The following assumptions have been made for the collection of the inventory data:

- The following data related to the first scenario derive from Base Protection measurements and analysis of the supply chain:
 - Weight of the produced part.
 - Transport of the raw materials used.
 - Production run time.
 - Molding press energy consumption.
 - Dryer energy consumption.
 - Drying time.
 - Data related to the tools used (type of material, weight of the raw material, weight of the mold and counter-mold, useful life).
 - Labour time .
- The following data derive from the Ecoinvent 3.1 database:
 - The energy consumption for the milling phase of the molds (for both the scenarios).
 - Inventory data related to transportation.
 - Inventory data related to input materials.
- Regarding the second scenario, the following data derive from CETMA measurements:
 - Energy consumption for the compression molding process.
 - Mold and counter-mold final weight.
 - Consumables weight.
- The transport of the materials used has been estimated considering the involved companies locations.
- The raw material weights of the aluminium molds have been estimated to be 30% higher than the weight of the finished molds.
- The impacts related to the production of the machines used to produce the parts were not considered; their useful life is much longer than the time required for a production run so their impacts would be negligible.
- The useful life and the disposal of the product were not considered.
- The dryer filter impacts were not considered.

All the inputs quantities are detailed in the next paragraphs.

8.2.1 Input materials

The main input material used in the first scenario is the thermoplastic compound for the injection molding process. Since no detailed information about the blend used were available, the raw material was considered to be constituted only by polycarbonate (which is the most present element in the blend). Regarding the second scenario, the main input material is constituted by the recovered prepreg scraps. Table 8.2 reports the details about the type and quantity of materials used.

Table 8. 1 inventory data related to the input materials

ITEM	MATERIAL	QUANTITY	
		SCENARIO 1	SCENARIO 2
Injection molding raw material	Polycarbonate	0,077 kg	-
Prepreg scraps	Prepreg	-	0,077
Prepreg PE release paper	Polyethylene (PE)	-	0,0078 kg
Release agent	Organic solvent	-	0,0075

8.2.2 Equipment used

The first scenario uses 40CrMnNiMo8-6-1 steel tools (mold and countermold). They have an estimated useful life of 10 years. Their weights data were supplied by Base Protection.

The second scenario uses aluminium tools. The final weights of the mold and the countermold were measured by CETMA. The raw material weight was estimated considering an increase of 30% on the weight of the finished molds.

Table 8. 2 inventory data related to the equipment

EQUIPMENT	ITEM	QUANTITY (kg)	
		SCENARIO 1	SCENARIO 2
Steel mold	Input steel	77,180 kg	-
	Mold final weight	62,409 kg	-
Steel countermold	Input steel	27,946 kg	-
	Countermold final	16,382	-
Aluminium mold	Input Aluminium	-	31,25 kg
	Mold final weight	-	25 kg
Aluminium countermold	Input Aluminium	-	31,25 kg
	Countermold final	-	25 kg

8.2.3 energy consumption

The energy consumption of the injection machine has been measured by the involved company. Since for every injection cycle four parts are realized, the energy consumption associated with the production of one toe cap has been calculated by dividing by four the energy consumption for one injection cycle. The energy consumption of the dryer has been measured too. Considering the total capacity of the dryer, the drying time, and the weight of the material used, the energy associated with the drying process was calculated according to equation 8.1.

$$D = \frac{w \cdot t \cdot E}{C} \quad (8.1)$$

With:

- D the energy consumption needed for the drying process of the material used for one product
- w the weight of the material used for a product (kg)
- C the capacity of the dryer (kg)
- t the drying time (h)
- E the energy consumption of the dryer per hour (kWh)

For the second scenario, the energy consumptions associated with the scraps cutting and peeling phases were calculated considering the rated power of the cutting and peeling machines and the weight of the prepreg scraps used. The energy consumption of the press for the compression molding process was measured by CETMA employers.

The energy consumptions data are reported in Table 8.3.

Table 8. 3 energy consumption inventory data

MANUFACTURING PHASE	QUANTITY	
	SCENARIO 1	SCENARIO 2
Cutting prepreg scraps	-	0,00038 kWh
Peeling prepreg scraps	-	0,0064 kWh
Curing compression molding		0,45 kWh
Storage energy consumption	-	0,066 kWh
Dryer energy consumption	0,013 kWh	
Curing injection molding	0,27 kWh	

8.2.4 Transportation

The transportation data used in this analysis have been estimated considering the geographical location of the Base protection suppliers. The transport of the release agent was not considered as, due to its low weight, the impact of its transport would have been negligible.

Table 8. 4 transport inventory data

TRANSPORTATION	DISTANCE (km)	TRANSPORTATION TYPOLOGY
Prepreg scraps	344	Truck 16-32 ton
Raw Aluminium and Steel	650	Truck 16-32 ton
Aluminium and Steel molds and countermolds	180	Truck 16-32 ton
Steel and Aluminium chips transport	650	Truck 16-32 ton
Polycarbonate	1000	Truck 16-32 ton

8.3 Life Cycle Impact Assessment (LCIA)

As in the previous LCA analysis, a complete evaluation of the environmental impacts associated with the production of the toe caps has been obtained by considering different environmental impact indicators:

- Cumulative energy demand (CED)
- Global warming potential (GWP)
- Midpoints and endpoints of the ReCiPe methodology.

8.4 Results and Discussion

SimaPro was used to create models of the described processes and to calculate all the impacts related to them. Considerations about the different environmental impacts associated with the two scenarios are reported in the next paragraphs.

8.4.1 Cumulative Energy Demand

Figure 8.3 and 8.4 show the results of the environmental evaluation of the two scenarios in terms of CED. The scenario 1 (injection molding) presents a lower environmental load than scenario 2 (scrap compression molding). More specifically, the injection molding scenario has a CED of 9,5 MJ, which is around 40% lower than the CED required for the compression molding production (which is 15,2 MJ).

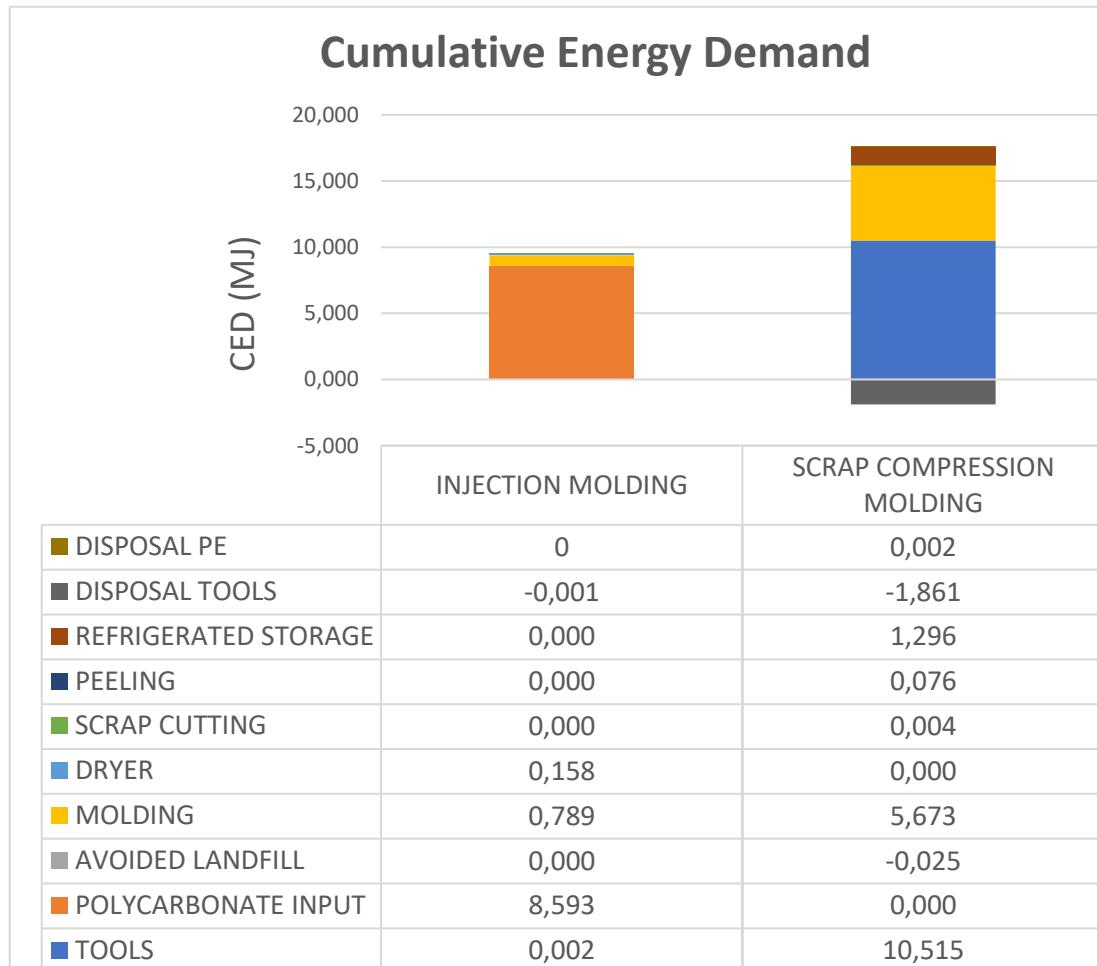


Figure 8. 3 LCIA in terms of Cumulative Energy Demand

The highest impacts of the first scenario are associated with the production of the raw materials used. In fact, the polycarbonate input accounts around 90% of the overall impacts (8,6 MJ out of a total of 9,5 MJ). The impact of the steel mold production is negligible due to their long-useful life expectancy (10 years).

In the second scenario, the raw material used has negligible impacts. The prepreg waste used have almost zero environmental impact: their use prevents them from being deposited in landfills and the preparation process and the transport have a CED value of 0,12 MJ (0,01% of the total impact). The impacts of the scrap compression molding production are mainly due to two production phases: the molds production and the molding phase, which together account around 95% of the impacts of the production phases. The molds are made of

Aluminium and their useful life has been considered to be of 750 molding cycle. Therefore, considering a two cavity mold, the impacts associated with the production of the tools have been divided only by 1500 parts. The molding phase in the second scenario requires a higher energy consumption (0,45 MJ) and a higher molding time (30 minutes) in comparison with the molding phase of the first scenario (which lasts only 65 seconds and has an energy consumption of 0,27 MJ). This behaviour can be attributable to the different types of material used; the thermosetting matrix prepreg used for the second scenario requires a time-consuming curing process to be hardened while the thermoplastic compound used in the first scenario gains rigidity simply by cooling down.

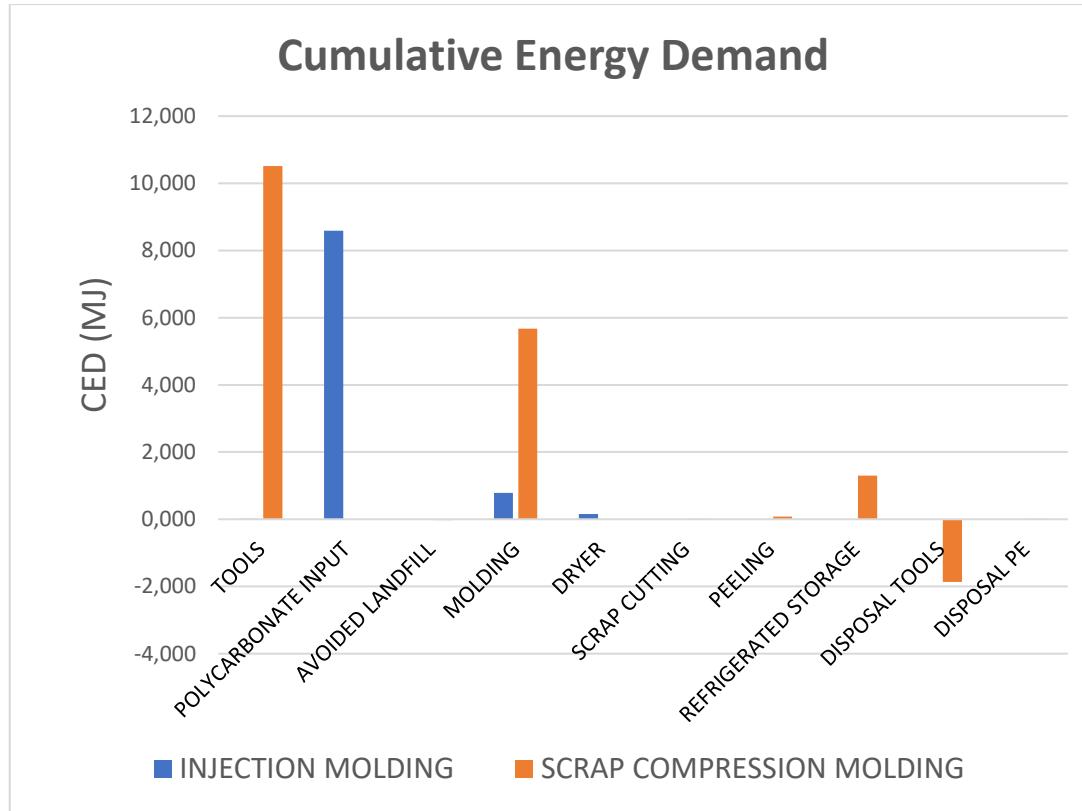


Figure 8. 4 CED for every production phase considered in the study

Excluding the impacts related to the molds productions and considering all the other processes, the second scenario would have a better environmental performance in terms of CED. Figure 8.5 shows how, if the aluminium molds service life could be extended by at least three times the present useful life, a break-even point would be reached for a production volume of about 4500 pieces. In the present situation, the injection molding production has a lower environmental load for any production volume.

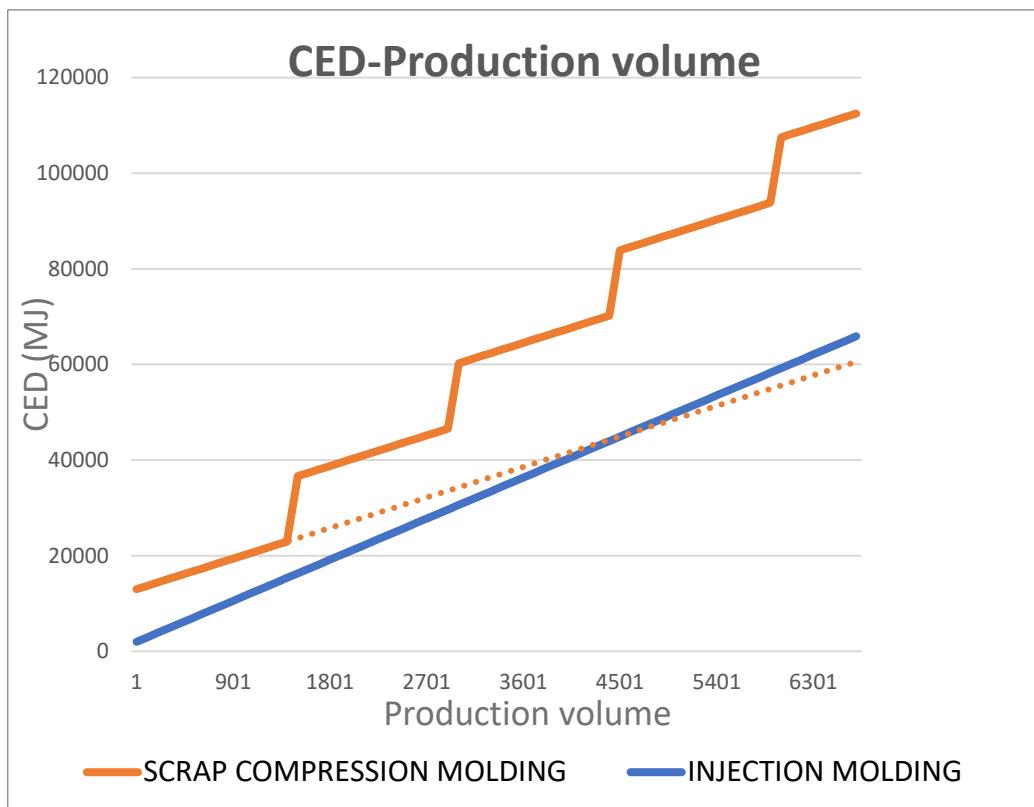


Figure 8. 5 CED – Production volume graph for the two scenarios

8.4.2 Global Warming Potential

The Global Warming Potential results expressed in “kg EQ of CO₂” are reported in figure 8.6. The impacts related to the injection molding production are equal to 1,14 kg eq of CO₂, whilst for the injection molding production are 0,63 kg eq of CO₂. The trend is very similar to the one observed for the CED, with the impacts of injection molding production being 40% lower than those of the alternative with recycled material.

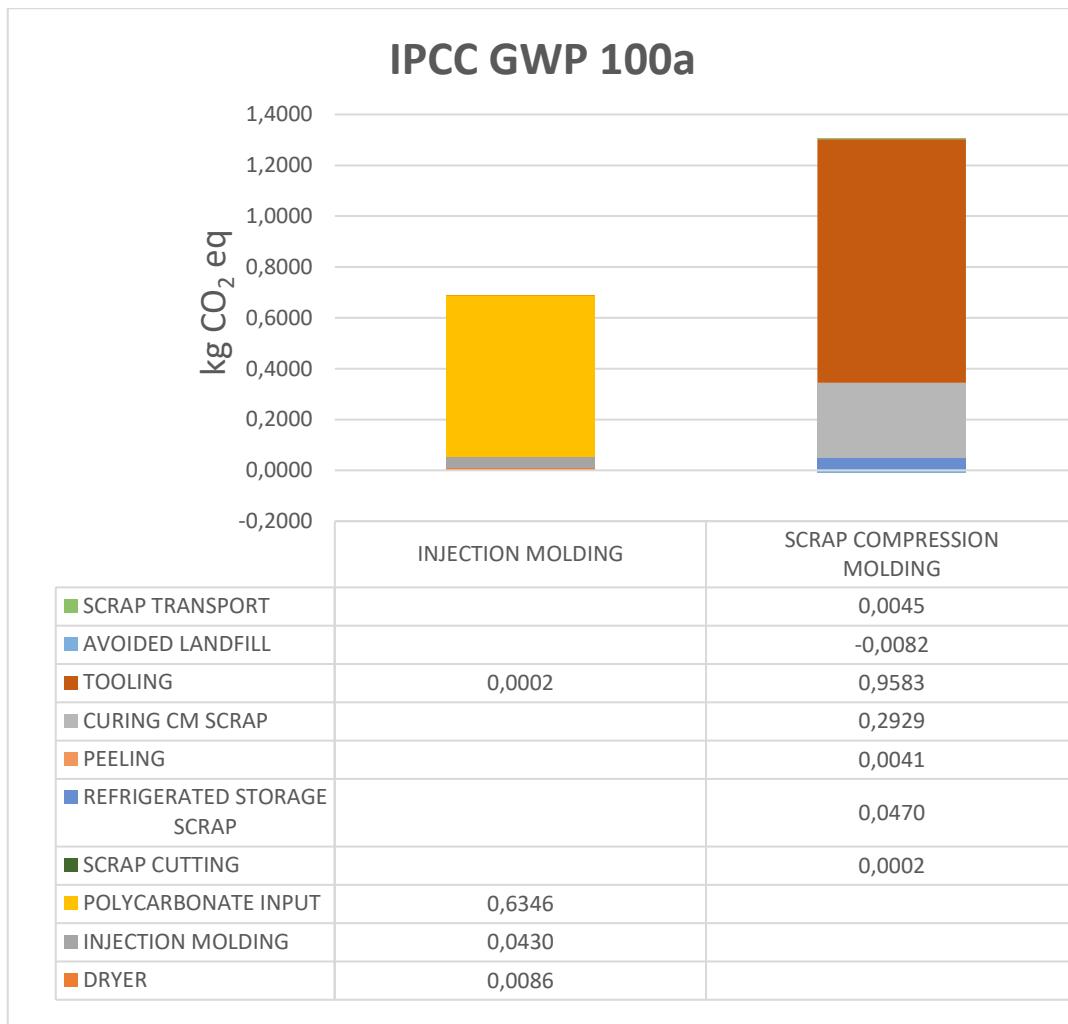


Figure 8. 6 LCIA in terms of GWP

8.4.3 ReCiPe

The results of the ReCiPe midpoint level are reported in Table 8.5. Since the impact categories have different units of measure, the data were processed to be able to create graphs easy to understand.

To create figure 8.7, each value was divided by the maximum value obtained for its impact category.

Table 8. 5 RCiPe midpoint categories

Impact category	Unit of measure	INJECTION PRODUCTION	SCRAP COMPRESSION MOLDING
Climate change	kg CO ₂ eq	6,70E-01	1,13E+00
Ozone depletion	kg CFC-11 eq	2,10E-07	4,60E-08
Terrestrial acidification	kg SO ₂ eq	2,02E-03	7,72E-03
Freshwater eutrophication	kg P eq	2,75E-05	2,91E-04
Marine eutrophication	kg N eq	3,82E-04	9,49E-04
Human toxicity	kg 1,4-DB eq	6,35E-02	3,04E-01
Photochemical oxidant	kg NMVOC	1,67E-03	3,90E-03
Particulate matter	kg PM10 eq	9,84E-04	2,69E-03
Terrestrial ecotoxicity	kg 1,4-DB eq	2,58E-05	2,24E-05
Freshwater ecotoxicity	kg 1,4-DB eq	2,27E-03	1,46E-02
Marine ecotoxicity	kg 1,4-DB eq	2,07E-03	1,37E-02
Ionising radiation	kBq U235 eq	1,07E-02	6,55E-02
Agricultural land	m ² a	2,47E-03	3,05E-03
Urban land occupation	m ² a	1,31E-03	8,54E-03
Natural land	m ²	1,52E-05	1,49E-04
Water depletion	m ³	4,47E-03	6,83E-03
Metal depletion	kg Fe eq	3,38E-03	3,63E-03
Fossil depletion	kg oil eq	1,91E-01	2,75E-01

The production with the recycled material has the highest environmental load for the majority of the midpoint categories. The two exceptions are the “ozone depletion” and the “terrestrial ecotoxicity” for which, due to the high contribution of the polycarbonate, the injection molding process has a higher environmental impact.

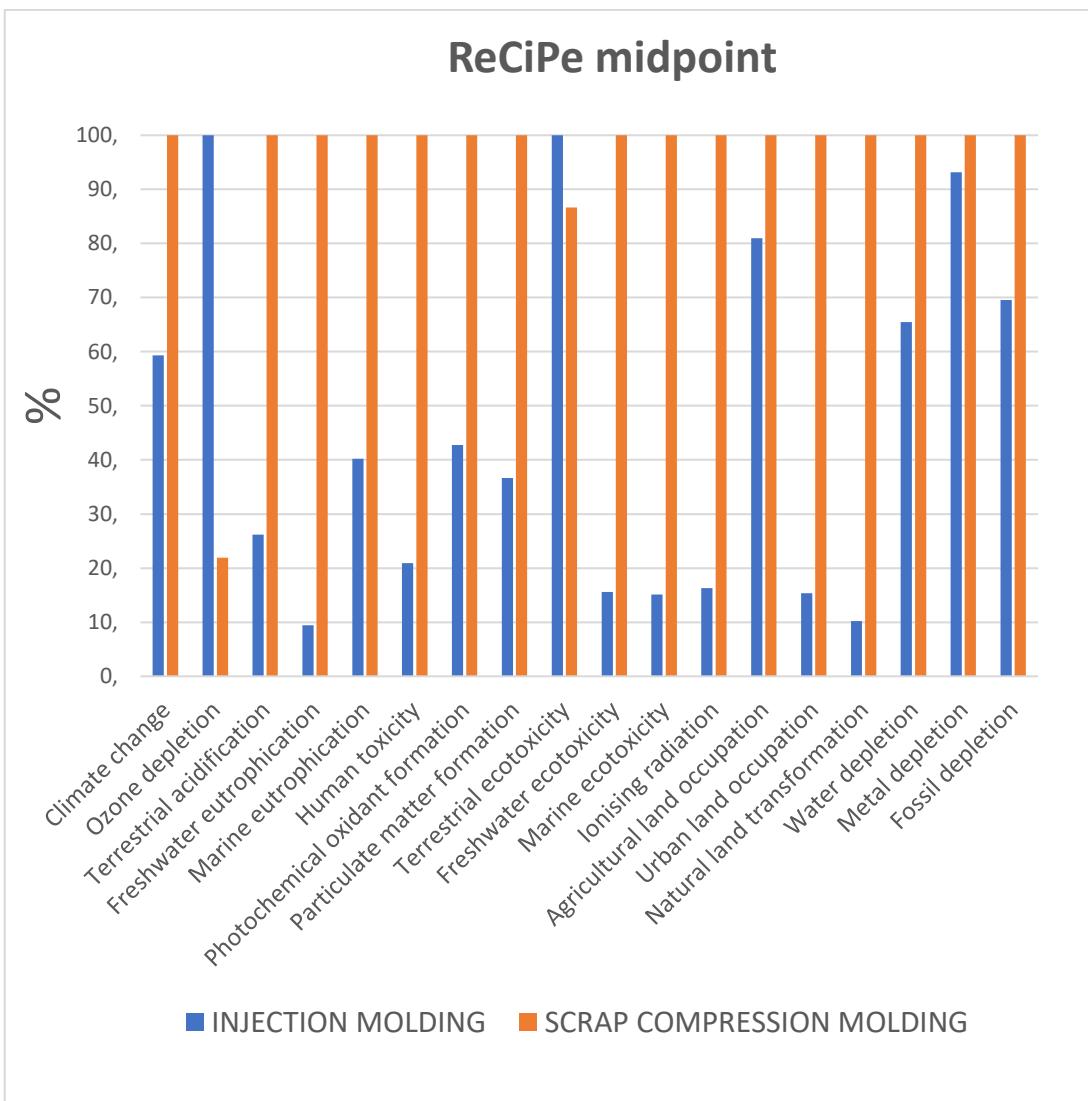


Figure 8. 7 LCIA in terms of ReCiPe midpoint

For figure 8.8, the data have been normalized (see paragraph 2.2.3). For all the categories with relevant normalized values, the first scenario has the best environmental performance. Figure 8.9 shows the contributions of each production phase for the normalized values of the second scenario. As for the CED and the GWP categories, the major contributions are given by the energy consumption of the curing phase and the raw materials used in the tooling phase.

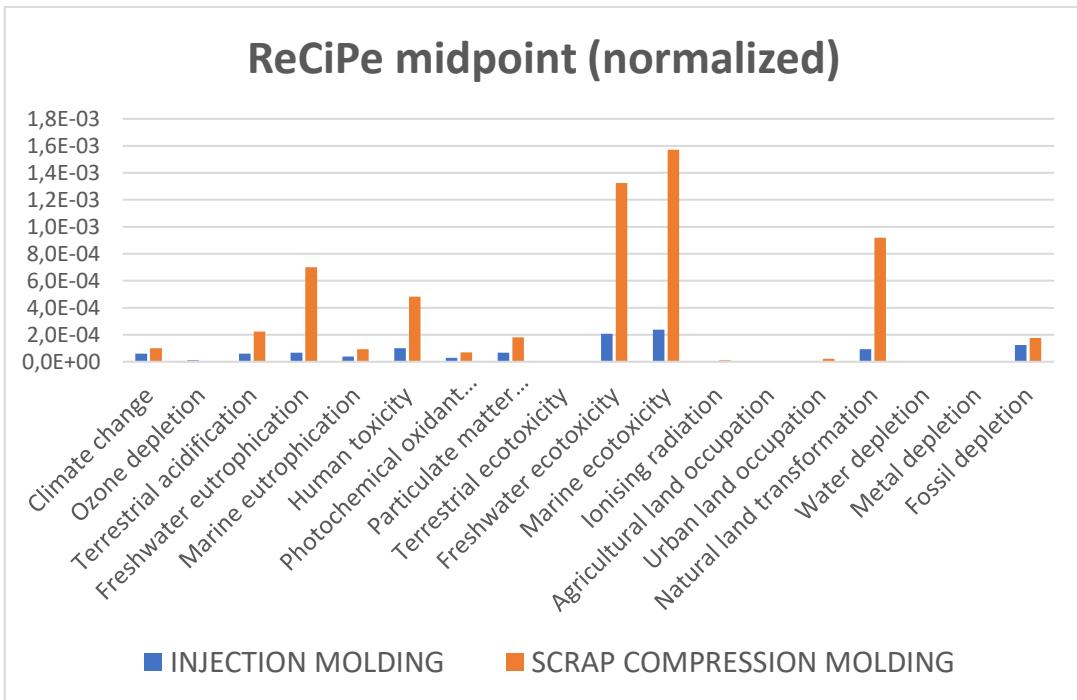


Figure 8. 8 ReCiPe normalized values for the two scenarios

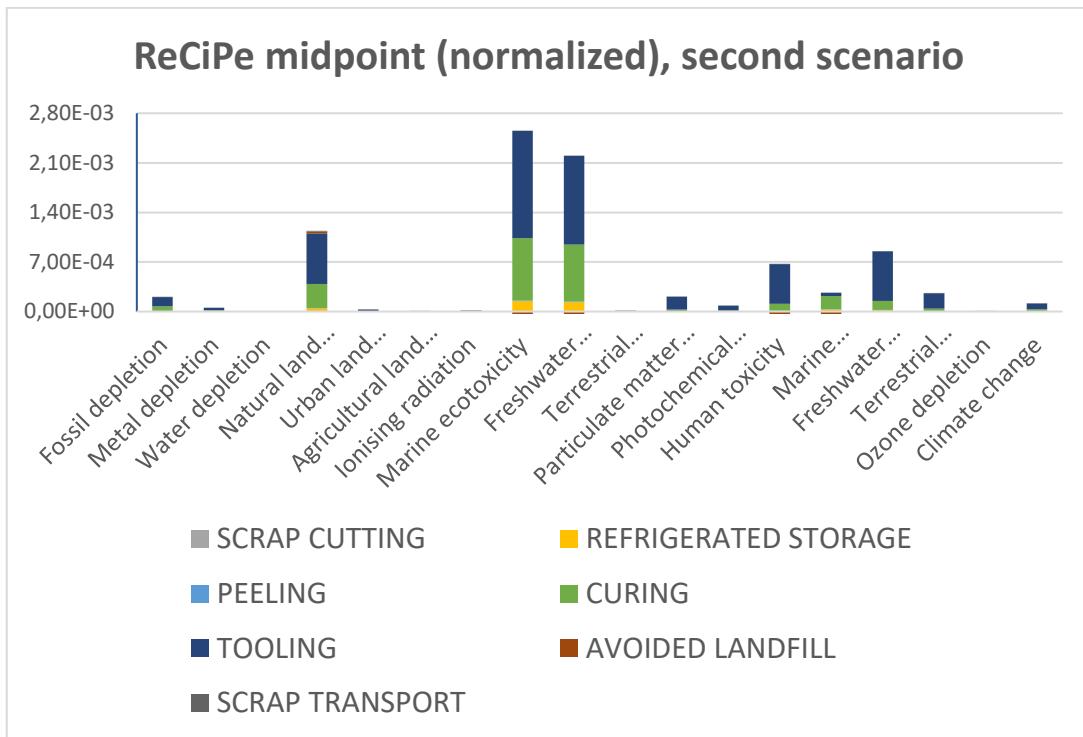


Figure 8. 9 contributions of each phase for the normalized value of the second scenario
ReCiPe midpoint

Lastly, an endpoint analysis has been carried out. The results confirm the trend found considering the CED and GWP indicators.

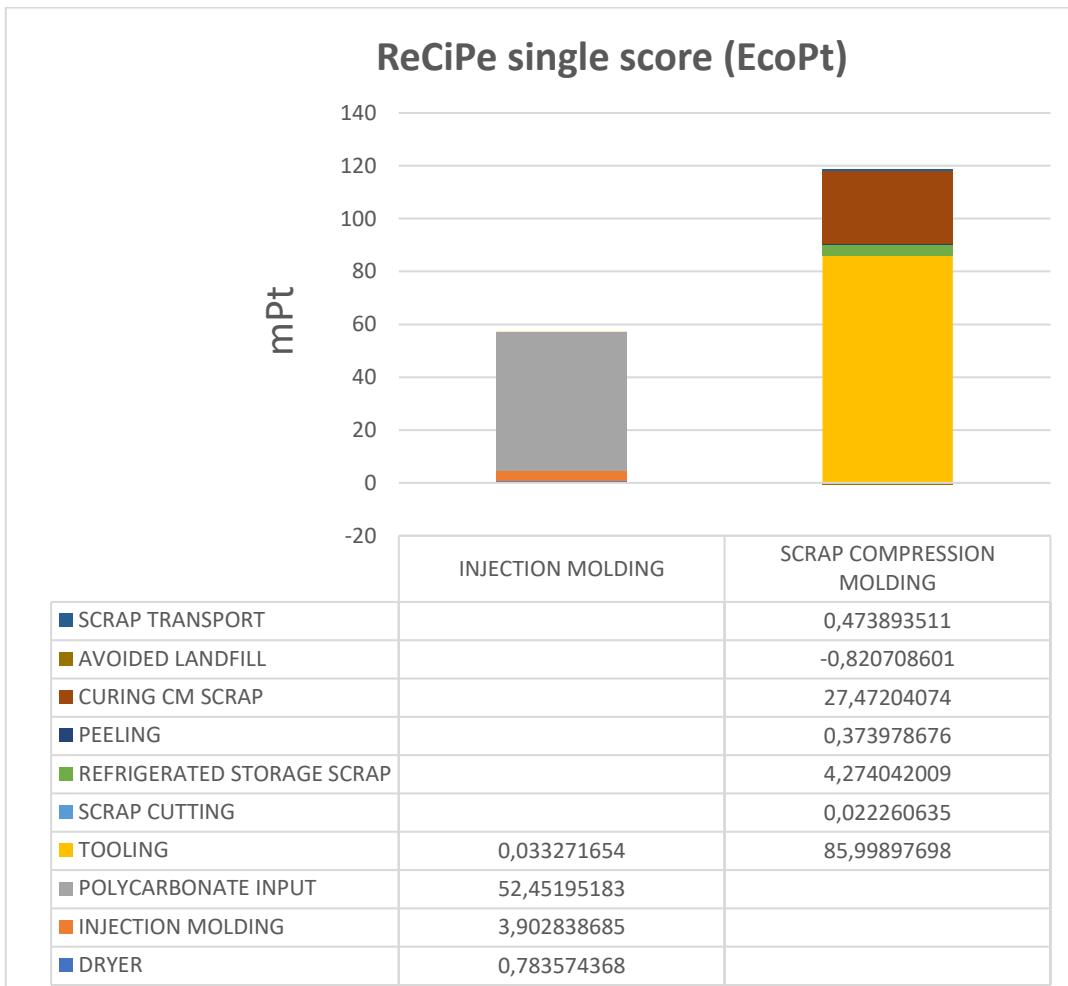


Figure 8. 10 ReCiPe single scores for the two scenarios

8.5 Life Cycle Cost (LCC)

As for the previous analysis, a Life Cycle cost study has been carried out to evaluate the economic performances of the two scenarios. The methodology applied is the same used for the analysis described in chapter 7.

The data used comes from several sources:

- Data about the materials, production time, and energy consumptions are the same used for the impacts analysis.
- Most of the data regarding the first scenario were provided by BASE Protection, so they come from industrial analysis and direct purchases. This category includes, for example the costs of the molds and the polycarbonate used.
- Regarding the second scenario, data have been provided mainly by CETMA. Moreover, since the second scenario is very similar to the production with recycled material made by HP Composites, some data were estimated considering the LCC data of the HP study.

Table 8.6 summarizes the cost inventory data for the two scenarios.

Table 8. 6 cost inventory data for the two scenarios

	COST	INJECTION	SCRAP
	COST FOR PRODUCT		
THERMOPLASTIC GRANULES	4,5 €/kg	0,35 €	0,00 €
PREPREG SCRAP	5 €/kg		0,39 €
PE WASTE DISPOSAL	0,3 €/kg		0,00 €
DRYER FILTER	76,00 €	0,00 €	
RELEASE AGENT	24,5 €/kg		0,18 €
LABOUR	20 €/h	0,08 €	5,00 €
ALUMINUM MOLD	815 €		0,54 €
ALUMINUM COUNTERMOLD	815 €		0,54 €
STEEL MOLD	8000 €	0,00 €	
STEEL COUNTERMOLD	8000 €	0,00 €	
PRESS CM	6000 €		0,02 €
FREEZER	600 €		0,00 €
INJECTION MOLDING PRESS	120000 €	0,01 €	
DRYIER	45000 €	0,00 €	
PRESS ENERGY CONSUMPTION	0,18 €/kWh		0,08 €
STORAGE ENERGY CONSUMPTION	0,18 €/kWh		0,01 €
DRYER ENERGY CONSUMPTION	0,18 €/kWh	0,00 €	
INJECTION MOLDING PRESS	0,18 €/kWh	0,01 €	
	TOTAL	0,46 €	6,77 €

The analysis shows that the Injection molding production has a much lower production cost than the compression molding alternative.

The scrap compression molding process is currently being developed by the CETMA employers. To conduct the analysis, they are using prepreg scraps obtained by their production processes but, as the process will be available for industrial production, the cut and peeled prepreg scraps will be provided by HP Composites. The selling price of the scraps will be around 5€/kg. At present, the toe caps are produced by a BASE supplier using a compound that has a cost of 4,5€/kg; so in this case, the recovered material has a slightly higher cost than the one currently used while in the previous study, the prepreg scraps were used in replacement of an 80 € per kg virgin material.

The main difference between the two scenarios is the labour cost. The injection molding production is highly automated and is suitable for high volume productions. The labour cost associated with it is of only 0,08 €/part. Instead, the compression molding production is under development and most of the processing is done manually; so, labour contributes for about 75% on the total cost of the second scenario.

Another difference between the two production processes costs concerns the molds. The steel molds used in the injection molding production have a useful life of 10 years, so the cost for each toe cap related to the molds is negligible. The aluminium molds are much cheaper than the steel ones but during their useful life they can produce only 1500 pieces, so the cost contribution of the molds for single toe cap produced is much higher than on the first scenario.

The energy consumptions, the dryer filters and the machines depreciation have a low contribution to the total costs.

Figure 8.11 and 8.12 show the total costs of the two scenarios as the production volume changes. For low production volumes, the major cost contribution in the two production processes is attributed to the molds. Since the aluminium molds have a purchase price that is considerably lower than the cost of the steel molds (around one-tenth), for low production volumes, the compression molding production is cheaper. However, due to the higher labour cost of the compression molding process, a break-even point is reached for a production volume of 2442 parts. At this level of development, the recovery production does not bring economic benefits to Base Protection because the actual production volume required for the toe caps is much higher than the breakeven point (BEP). An automation of the CM process, and a consequent reduction of the labour cost, would lead to a higher value of the break-even point. If the involved companies manage to increase the BEP up to a value higher than the actual toe caps production volume, the reuse of the prepreg waste will bring economic benefits to Base Protection.

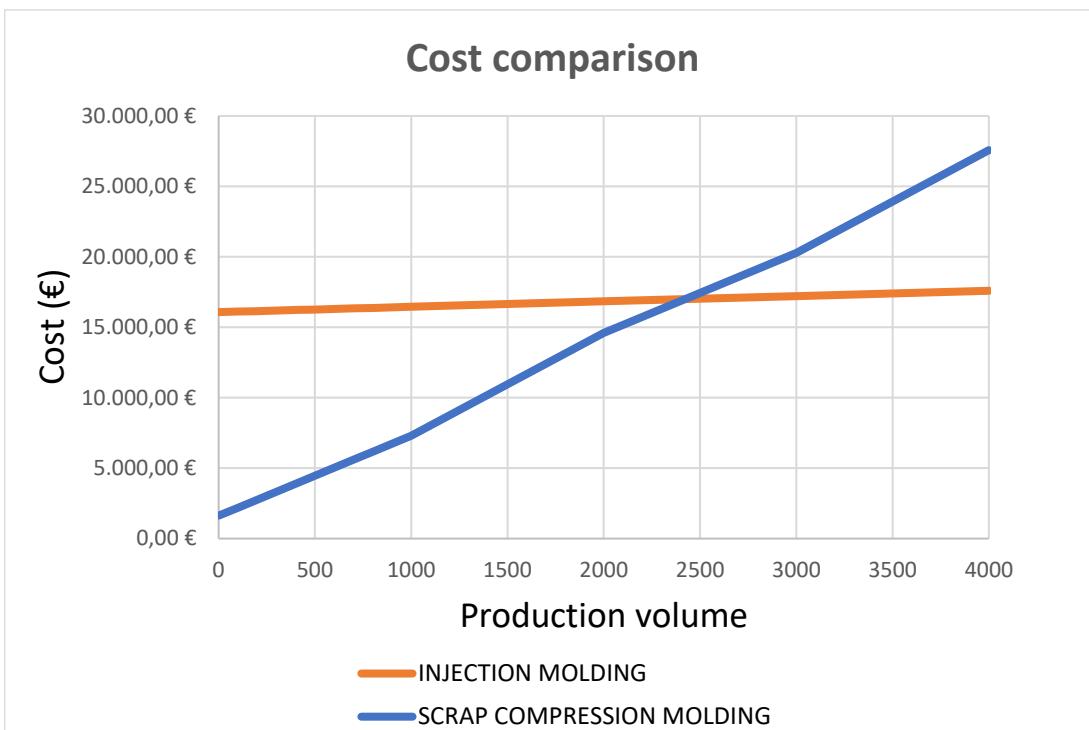


Figure 8. 11 Total cost vs production volume for the two production processes

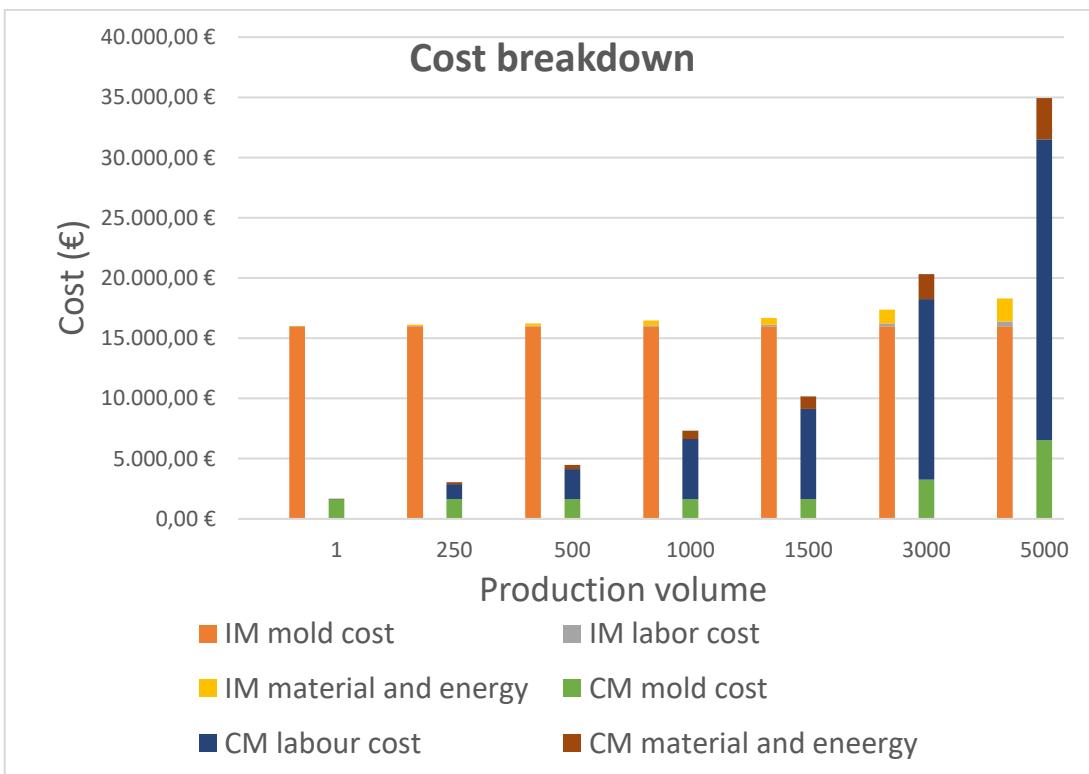


Figure 8. 12 Cost breakdown for the two scenarios

CHAPTER 9

CONCLUSIONS

Weight reduction achieved with composite materials can, in some applications such as aerospace and automotive, provide a substantial reduction in life cycle energy use and GHG emissions. On the other hand, CFRPs products manufacturing is usually an energy intensive process, mainly due to the energy required for CFs production. Since the market of carbon fiber reinforced polymer is continuously growing, finding sustainable end-of-life options and recycling methods for composite products has become a necessity. EU legislation is becoming more severe for what concerns the disposal of waste, acting as a driving force for the development of efficient recycling methods. Currently, several recycling techniques are available (mechanical, thermal, and chemical recycling) and they can provide a strong reduction of the environmental impacts. For example, a study conducted by Meng et al, estimated a reduction of Primary energy Demand (PED) equal to -495,5 MJ per kg of CFRP waste recycled by mean of fluidised bed recycling process. Even if the recycling processes have better environmental performances than other options like landfill or incineration, from the economic point of view they are not always preferable.

This study analysed the environmental and economic behaviour of a new recycling process for uncured thermoset matrix / carbon fiber reinforced prepreg scraps. Two LCA analysis were carried out to compare the manufacturing of composite components with the recycled materials to traditional production processes.

The first LCA analysis evaluated the environmental performances of three different production processes for a CFRP sample. The study showed considerable environmental benefits associated with the new recovery process. The new recycling system allows to recover 100% of the prepreg waste and has negligible environmental impacts. Using the recovered scraps it is possible to completely avoid virgin prepreg, which constitutes the major contribution on the total impacts of the traditional production processes (around 70%). In term of Cumulative Energy Demand, the recycling process can save 601,5 MJ per kg of recovered prepreg scraps, while in terms of GWP the saving is 37,4 kg eq CO₂ per kg of CFRP recovered. Comparing the environmental benefits of the analysed process with a previous study by Meng et al, it results that in terms of GWP, the new system can save 44% more of the CO₂ emissions than the fluidised bed recycling process (which in that study emerged to be the best recycling alternative available). For low production volume, the manufacturing with the recycled material presents a higher environmental load due to the heavier molds. Therefore, as higher production volumes are considered, two break-even points are reached (for 27 and 129 parts produced) and the production with recycled material become the best environmental alternative. The impact assessment carried out considering the ReCiPe method confirms the trend found as CED and GWP indicators are concerned.

In the first analysis, the recycling process also leads to economic saving. For low production volume, the mold costs are higher in the recycling scenario than in the other two due to their

higher weight. For a production volume of at least 49 parts, the economic saving related to the reuse of waste materials makes the recycling alternative the less expensive. Economic saving is expected to increase as heavier products will be produced in the future.

The second LCA analysis evaluated the environmental impacts of the production processes of toe caps for work footwear. In this case, the recycled material is used to replace a thermoplastic blend mainly composed by polycarbonate; the virgin material used has a considerably lower environmental impact in comparison with the prepreg used in the first analysis.

The production with scraps has two main impact contributors: the energy consumption of the molding phase and the production of the aluminium tools. The total impacts of the new production process are higher than the ones of the injection molding production (in terms of all the considered impact indicators). Increasing the useful life of the aluminium tools would reduce their contribution to the total environmental load, leading to a reduction of the impacts of the compression molding scenario. In this way, in terms of CED, for production volume higher than 2442 parts (the break-even point), the scrap compression molding process would have a lower environmental impact than the injection molding process. The ReCiPe and the GWP methods show similar results. Regarding the costs analysis, the scrap production is the most expensive. This is due mainly to the labour required for the manual lay-up. The injection molding production is highly automated while the compression molding process, since it is still in a development phase, relies on manual work for most of its phases. Moreover, in this case, the waste material does not bring economic saving since it is used to substitute a cheap virgin material. As the compression molding process will be automated, a new LCC analysis will be carried out to evaluate for which production volumes the use of waste material can bring economic benefits.

The new recycling process, developed within the CIRCE projects, has shown a great potential for the reduction of costs and environmental impacts of CFRP components manufacturing. The biggest benefits are obtained when the recovered scraps are used to substitute a high-environmental impact virgin material such as the prepreg. In that case, the impacts reduction is higher than most of the common recycling methods available.

Future work will be focused on the investigation of composite industrial applications, such as the production of automotive components, so that the recovery process efficiency will be analysed in a more practical situation with a greater amount of primary data.

Sunto in italiano

Questa tesi ha lo scopo di valutare gli impatti ambientali associati a un nuovo processo di recupero per sfridi di materiale composito preimpregnato non polimerizzato. Lo studio è collocato all'interno del progetto CIRCE, nato dalla collaborazione di cinque aziende italiane e co-finanziato dall' Unione Europea tramite il programma LIFE. L'obiettivo di questo progetto triennale è di sviluppare due nuove macchine che permettano di recuperare e preparare gli scarti prodotti durante la fase di taglio del prepreg per poterli riutilizzare per nuovi processi produttivi. Durante la fase di taglio, infatti, un quantitativo solitamente compreso tra il 20 e il 50% in peso del prepreg diventa direttamente uno scarto, senza mai essere effettivamente usato. Attualmente, gli scarti di prepreg prodotti dalle produzioni di HP Composites vengono depositati in discarica. Visto l'elevato impatto ambientale e l'elevato costo associato alla produzione del prepreg, l'utilizzo di questi scarti è una necessità non solo ambientale ma anche economica.

La prima delle due nuove macchine sviluppate permette di tagliare gli scarti in pezzi di circa 5x5 cm. Forma e dimensione possono variare a seconda dei processi di taglio precedenti effettuati sul rotolo di prepreg vergine. La seconda macchina permette di eliminare il release paper di polietilene dal prepreg di scarto (macchina di spellicolamento) in modo da rendere utilizzabili gli scarti come materiale di recupero. Se non immediatamente utilizzati, gli scarti preparati in questo modo vanno tenuti in uno congelatore industriale in modo da evitare la completa cura della resina termoindurente che costituisce la matrice del prepreg. Il materiale di recupero ha diverse possibili destinazioni; potrebbe essere utilizzato direttamente da HP Composites (che si occupa anche della preparazione al riutilizzo degli scarti) per la produzione di componenti per il settore automotive. Altre possibili applicazioni in fase di studio sono la produzione di puntali per scarpe antinfortunistiche e freni carboceramici.

Nei primi capitoli di questa tesi sono stati introdotti gli strumenti, i processi e i materiali utilizzati nell'analisi. Il primo capitolo introduce il concetto di progettazione integrata (concurrent engineering) e Design per l'ambiente. Il secondo capitolo spiega nel dettaglio lo strumento utilizzato per valutare gli impatti ambientali di processi produttivi studiati: il Life Cycle Assessment. I capitoli 3 e 4 introducono i materiali e i processi produttivi considerati nelle analisi degli impatti dei capitoli successivi. Il capitolo 5 è una panoramica dei sistemi di smaltimento di rifiuti in materiale composito attualmente disponibili. Il capitolo 6 introduce il programma del progetto CIRCE.

I due capitoli successivi presentano due analisi LCA, condotte per produzioni relative ad HP Composites e BASE. Il capitolo 9 presenta le conclusioni dello studio.

L'analisi LCA, come descritto nelle norme ISO 14040-14044, si compone di 4 fasi:

1. Definizione dell'obiettivo dello studio, dell'unità funzionale, degli scenari considerati e dei confini del sistema.
2. Life Cycle Inventory (LCI); consiste nella raccolta dei dati relativi agli inputs e agli outputs con impatti rilevanti all'interno dei confini del sistema.

3. Life Cycle Impact Assessment (LCIA); in questa fase, vengono scelte delle categorie di impatto per ottenere una visione completa degli impatti dei processi considerati. Tramite opportune valutazioni, gli inputs e gli outputs dei sistemi sono associati a degli impatti secondo le categorie scelte. Si ottengono così dei valori rappresentativi degli impatti ambientali.
4. Analisi e discussione dei risultati; i risultati ottenuti nel LCIA vengono analizzati e si identificano i fattori ambientali più rilevanti. Infine, vengono riportate le conclusioni, le limitazioni e le raccomandazioni utili per diminuire gli impatti associati al sistema studiato

La prima analisi effettuata confronta la produzione di un provino di materiale composito (matrice polimerica termoindurente rinforzato con fibre di carbonio) tramite tre diversi processi produttivi. La resistenza a trazione del provino è uguale per tutti e tre i processi produttivi nonostante usino materiali di partenza differenti; il peso dell'unità funzionale, quindi, varia con il processo produttivo considerato. Il primo e il terzo scenario (una produzione in autoclave e una per compression molding) utilizzano del preimpregnato vergine per la produzione della parte. Il secondo scenario (una produzione sotto pressa simile alla prima) utilizza il materiale di recupero ottenuto dagli scarti di prepreg. Dopo la raccolta dei dati, gli impatti ambientali sono stati valutati considerando diversi indicatori: il CED, il GWP e i ReCiPe midpoint ed endpoint. Nel secondo scenario, essendo il materiale in ingresso a impatto praticamente nullo, gli impatti complessivi sono inferiori rispetto alle altre due alternative. Dato l'elevato impatto della produzione delle fibre di carbonio, negli scenari 1 e 3, il contributo maggiore per gli impatti è sempre associato a prepreg vergine utilizzato. Il processo di recupero degli scarti ha un impatto ambientale praticamente trascurabile e garantisce una riduzione degli impatti di 601,5 MJ (indicatore CED) e 37,4 kg eq CO₂ (indicatore GWP) per kg di scarto di prepreg recuperato. Confrontando questi risultati con precedenti studi, emerge che il nuovo processo di riciclo ha performances ambientali superiori alla maggior parte dei sistemi di riciclo per composti a matrice termoindurente attualmente presenti sul mercato. Ad esempio, garantisce una riduzione delle emissioni equivalenti di CO₂ superiori per il 44% alla riduzione ottenuta dal sistema di riciclo a letto fluido (confrontando i risultati con uno studio di Meng et al). I risultati degli indicatori ReCiPe sono in linea con quelli del CED e del GWP. Successivamente, per valutare la convenienza economica del processo, è stata effettuata un'analisi dei costi (Life Cycle Costing). Grazie al risparmio ottenuto dalla sostituzione del preimpregnato vergine con quello di recupero, il secondo scenario risulta il più economico. Inoltre, valutando il risparmio al variare del peso della parte realizzata, si prevede un aumento dei benefici economici associati al secondo scenario all'aumentare del peso del prodotto. Questo sarebbe il caso di produzioni industriali di parti per il settore automotive che sicuramente avrebbero un peso superiore a quello del provino considerato in questa analisi (che ha un peso compreso tra 60 e 70 gr).

La seconda analisi LCA riguarda la produzione di puntali per scarpe antinfortunistiche. Attualmente, questi elementi vengono prodotti per stampaggio a iniezione (IM) utilizzando un materiale termoplastico; BASE Protection, in collaborazione con CETMA, sta valutando di produrre i puntali utilizzando gli scarti di prepreg in una produzione per compression molding (CM). Queste due possibili produzioni sono state considerate nell'analisi degli impatti. Come nel caso precedente, dopo la raccolta dati da diverse fonti (industriali, di

letteratura scientifica e misurazioni), gli impatti ambientali sono stati calcolati secondo diversi possibili indicatori. Contrariamente alla prima analisi, l'utilizzo di materiale riciclato non garantisce una riduzione degli impatti ambientali. Questo è dovuto principalmente agli elevati contributi della produzione degli stampi e della fase di cura della produzione per CM. Per sviluppi futuri, ridurre gli impatti associati alla produzione degli stampi potrebbe portare ad una convenienza ambientale del processo con materiale di riciclo. La successiva analisi dei costi ha mostrato come, a causa della scarsa automatizzazione del processo sviluppato da CETMA e dell'importante contributo della manodopera, la produzione per CM ha un costo notevolmente superiore rispetto all'alternativa per IM. In questo caso, inoltre, il prepreg di scarto sostituisce un materiale dal costo contenuto mentre nell'analisi per HP sostituiva un materiale vergine con un costo al kg di 80 €, e quindi non c'è un risparmio considerevole associato alla diversa materia prima. Per sviluppi futuri, un'automatizzazione del processo potrebbe rendere la nuova produzione economicamente preferibile.

Il processo di riciclo sviluppato dal progetto CIRCE ha mostrato un grande potenziale per la riduzione degli impatti e dei costi dei processi produttivi di materiali compositi. Ulteriori analisi saranno necessarie per avere una visione più completa per quanto riguarda la produzione di parti per applicazioni industriali. Lo studio in collaborazione con CETMA e BASE potrà essere aggiornato quando ci sarà una maggiore ottimizzazione e automatizzazione del processo, in modo da per riconsiderare i costi e gli impatti ambientali.

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