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Mechanical recycling of polymer-based composites

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Declaration

I hereby declare that, the contents and organisation of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

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Abstract

In the last decades environmental issues have assumed a key role in the worldwide community. In fact, it has been understood that economic growth is not sufficient to guarantee the progress of a community, if it does not consider all the conditions surrounding a specific technological process: from the supply of the raw materials to environmental pollution, from energy consumption to the production of waste.

In this perspective, in 2010 the European Union launched a ten-year strategy called Europa2020 which sets five economic, social and environmental objectives aimed at creating the conditions necessary for sustainable growth. In particular, the third objective, concerning climate change and energy sustainability, foresees the reduction of greenhouse gas emissions by 20% compared to 1990.

In the automotive sector, this push for sustainability has often resulted in the production of lighter components, which allow to reduce fuel consumption and therefore pollutant emissions. The need for lighter components has leads to a gradual replacement of conventional materials with thermoplastic matrix composites.

The high amount of automotive end-of-life composite component in landfills is an issue that car manufacturers must face, since their recycling is mandatory. In fact, according the European Directive at least 95% by weight of the vehicle must be reused and recovered.

The purpose of this thesis is to show how mechanical recycling of glass fiber reinforced thermoplastic composites is one of the most recommended and simplest

methods to obtain a material with mechanical properties useful for different applications. In particular, two different types of composite waste were recovered, both made of polyamide matrix reinforced with glass fiber: an end-of-life vehicle component and processing scraps from the thermoforming process.

The thesis is structured in several chapters. The first chapter is an overview of the European legislation currently in force in Europe regarding waste, with a focus on end-of-life vehicles. The second chapter depicts the existing literature on the recycling of composite materials both for experimental approaches and for the strategies currently used on an industrial level. The third chapter describes the properties of polyamide matrix composites reinforced with glass fibers. Chapter 4 illustrates the materials, the mechanical recycling processes and all the characterization methods used. In chapter 5 all the results obtained from the mechanical recycling of an end-of-life vehicle component are reported, while the results relating to the recycling of production scraps are described in chapter 6.

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Chapter 1

European legislation on waste

1.1 How to recycle waste

European directive 2008/98/CE establishes a "waste hierarchy", an order of priority of the policies to be adopted in the field of waste management [1]. The waste hierarchy shows in Figure 1.1 consists of the following steps:

- **Prevention**: consists of the measures taken before a substance, product or material has become a waste. First of all, it is necessary to reduce the quantity of waste, by reusing the product or extending its life span. Secondly, to reduce the negative impacts of waste on the environment and human health. Finally, to reduce the content of dangerous substance in materials and product.

- **Preparing for re-use**: the operations of checking, cleaning and repairing, through which products or components of products that have become waste are prepared so that they can be reused without any other pre-treatment. Reuse implies that the product is re-used for the same purpose for which it was conceived.

- **Recycling**: any recovery operation through which waste materials are reprocessed to obtain products, materials or substances to be reused for their original or other purposes. It includes the reprocessing of organic material but not energy recovery or reprocessing to obtain materials to be used as fuels.

- **Other recovery**: e.g. energy recovery: any operation whose main result is to allow waste to play a useful role by replacing other materials that would otherwise have been used to perform a particular function or to prepare them to perform this function, within the plant or in the economy in general. Use principally as a fuel or other means to generate energy.

- **Disposal**: any operation other than recovery even when the operation has as a secondary consequence the recovery of substances or energy. The disposal in landfills and incineration are included in the disposal operations.

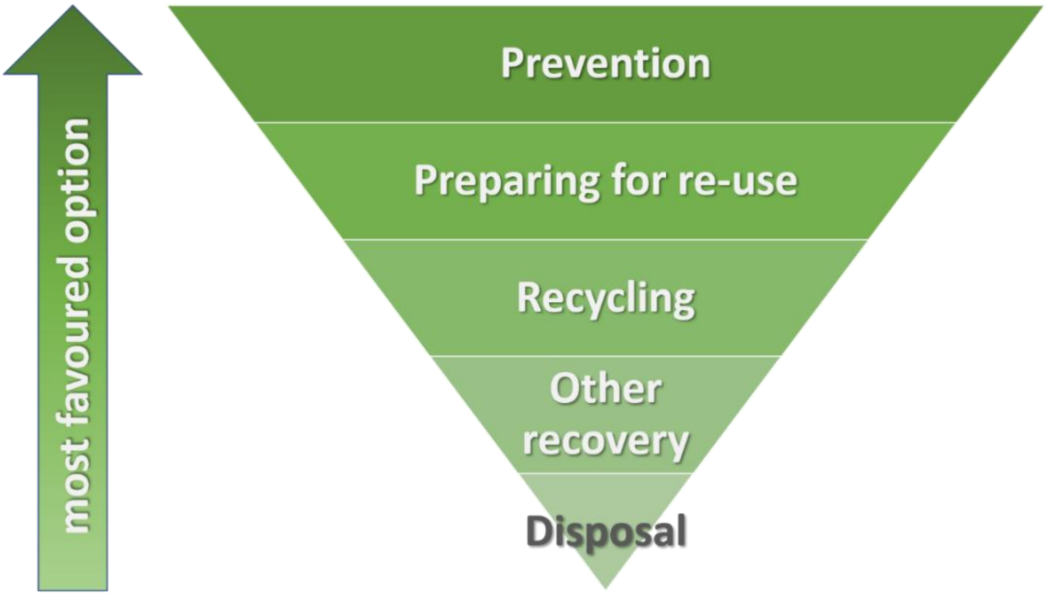


Figure 1.1 Waste hierarchy proposed by the European directive 2008/98/CE: from the most favoured option (prevention) to the least one (disposal).

Therefore, all the materials or products considered waste must be treated appropriately following the order of priority of the waste hierarchy. In the industrial sector it becomes essential to understand which products should be considered waste and which only by-product. From this point of view, directive 2008/98/CE defines waste in this way:

> *'waste' means any substance or object which the holder discards or intends or is required to discard* [1]

A substance or product resulting from a production process is to be considered a by-product if:

- The primary purpose of the process is not the production of this article
- It is certain that the substance or object will be further used
- the substance or object can be used directly without any further treatment other than normal industrial practice.
- the substance or object is produced as an integral part of a production process
- the substance or object fulfils all requirements regarding the health and environmental protection

Furthermore, the directive gives a whole series of definitions which are fundamental and to which many other European directives refer. It defines hazardous waste, or the characteristics that the waste must have to be considered hazardous: flammable, irritant, harmful, toxic, carcinogenic, corrosive, infectious, mutagenic etc.

It should be emphasized that the directive defines organic waste as biodegradable waste, thus excluding all non-biodegradable plastics that from a chemical point of view are organic compounds.

It is also important to establish when a waste ceases to be considered waste. This happens when the object is used for specific purposes, respects existing standards, there is a market for this object and its use will not lead to negative impacts on the environment.

As regards the re-use and recycling of waste, the directive requires Member Countries to establish separate waste collection at least for the following waste:

paper, metal, plastic and glass. It also encourages Member States to take the necessary measures to achieve the following targets:

- *by 2020, the preparing for re-use and the recycling of waste materials such as at least paper, metal, plastic and glass from households and possibly from other origins as far as these waste streams are similar to waste from households, shall be increased to a minimum of overall 50 % by weight*
- *by 2020, the preparing for re-use, recycling and other material recovery, including backfilling operations using waste to substitute other materials, of non-hazardous construction and demolition waste excluding naturally occurring material defined in category 17 05 04 in the list of waste shall be increased to a minimum of 70 % by weight*

Therefore, the push towards recycling starts from the separate collection of urban waste. Since the European directives require the Member States to carry out separate collection, the subsequent problem is to ensure that this waste once differentiated are destined for the dedicated sorting plants and do not end up in landfills.

To that end, the European directive 2018/850 modifies the 199/31/CE concerning waste landfills, further increasing the restrictions on the landfill of waste. In particular, it prohibits that municipal waste collected for recycling ending up in landfills. The directive requires European Member States to take appropriate measures to allow, starting in 2030, to prohibit the landfilling of all waste suitable for recycling.

In addition to reducing the landfilling of waste suitable for recycling or recovery, the directive aims to prevent the negative effects on the environment due to the presence of landfills. These include pollution of surface and ground water, soil and air pollution, as well as risks to human health.

The directive provides for the prevention, recycling and enhancement of waste, as well as the reuse of materials and energy recovered, in order to save natural resources and reduce land use. In particular, relevance is given to incineration, composting and reclamation treatment, as well as the "polluter pays" principle and the pollution generated by landfills.

Specifically, the directive provides that biodegradable urban waste to be landfilled must be reduced from 75% to 35% of the total weight of biodegradable urban waste produced. And that by 2030 all waste suitable for recycling or other recovery is not allowed in landfills. By 2035 the amount of urban waste landfilled is reduced to 10%.

All waste to be landfilled must be treated, or subjected to physical, thermal, chemical or biological processes that modify the characteristics of the waste in order to reduce its volume or dangerous nature and facilitate its transport or recovery. Landfills cannot accept used tires, liquid, flammable, explosive or corrosive waste.

1.2 How to recycle end-of-life vehicles

Since every year end of life vehicles (EoLV) in the European community produce 8-9 million tons of waste (Figure 1.2), it was necessary to organize a Community legal framework that guarantees:

- vehicle design for recycling and reuse
- the requirements for collection and treatment facilities
- reducing the environmental impact of vehicles
- the proper operation of the European internal market

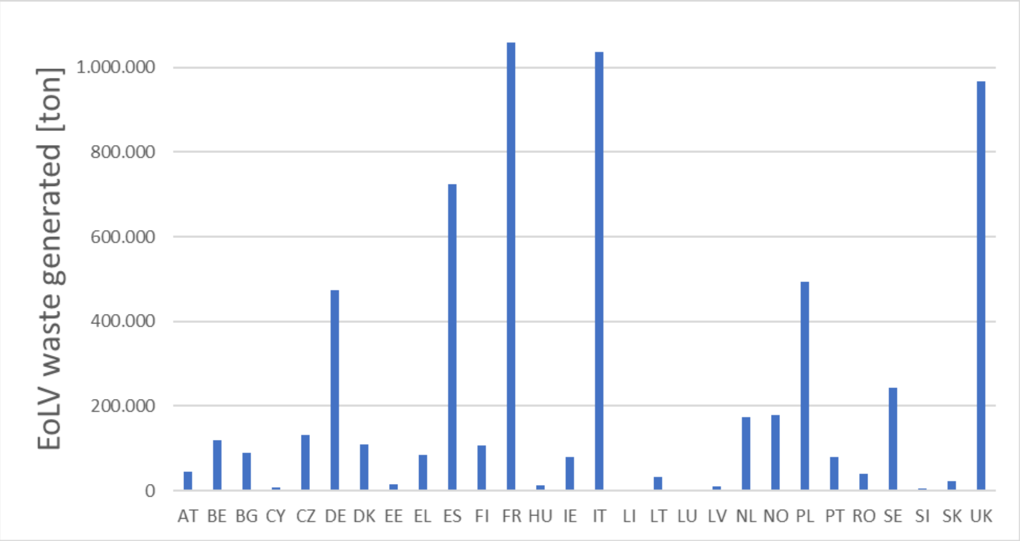


Figure 1.2 Generation of end-of-life waste by country in 2015 in tonnes

The directive 2000/53/CE aims to standardize the various national measures concerning end-of-life vehicles (EoLV). The directive applies not only to vehicles intended as a single product, but also to all the components, materials and replacement parts that constitute them. The indication of the directive in terms of prevention, collection, treatment, reuse and recycling of end of life vehicles are summarized below:

- **Prevention**: first of all, the directive operates from the perspective of prevention. To this end, it encourages manufactures to limit the use of hazardous substances and for vehicles currently in production. In this regard, the use of highly polluting and dangerous elements such as lead, mercury, cadmium and hexavalent chromium is prohibited and allowed only for specific applications. The list of these applications has been revised several times since 2000 and includes the use of cadmium only in thick film pastes, mercury in discharge lamps and instrument panel displays, hexavalent chromium in corrosion preventive coatings and absorption refrigerators in motorcaravans. As concern lead there are more authorized applications and they concern its use as an element in steel or aluminium or copper alloys. As free element it can be used in batteries, for welding, as vibration dampers, in glass or ceramic matrix compound except glass in bulb and glaze of spark plugs. Furthermore, if these heavy metals can be removed before further treatment, they must be properly marked and labelled [2]. Vehicle design must consider all aspects concerning demolition, reuse, recovery and above all recycling of end-of-life vehicles and their components and materials. On the other hand, vehicle and component manufacturers must commit themselves to providing more and more recycled material in order to allow the development of a market for recycled materials. Here the legislation focuses on a fundamental aspect: the recycling of material is possible only if a supply chain is created, which allows the systematic recovery of waste. Therefore, even in the case of end-of-life vehicles, the formation of a production chain of car waste is necessary in order to generate a market for recycled materials. The presence of a market makes recycling advantageous since the waste passes from being a cost for disposal to a saleable resource; and economic as the price of recycled material would fall further and further.

- **Collection**: the creation of a chain of end-of-life vehicle waste is connected first and foremost with the presence of an adequate number of collection facilities in the territory of the Member States. Furthermore, it must be guaranteed that all end-of-life vehicles are delivered to authorized treatment facilities. To allow this, the directive requires the Member states, if they were not already in possession, of setting up a system that makes it necessary to present a certificate of destruction for the deregistration of the end-of-life vehicle from the automobile register. In fact, only when the vehicle owner delivers the car to a treatment plant is the certificate issued. The vehicle must be delivered to the treatment plant free of charge for the car owner. For this purpose, the producers must meet all or a significant part of the costs associated with the implementation of this measure. To make everything integrated, the directive declares that Member States must accept the certificate of destruction issued by other EU states. Car manufacturers, every time they place a new type of vehicle on the market, must provide all the information necessary for the proper disposal of the vehicle within six months of placing them.

- **Treatment**: as regards the treatment of end-of-life vehicles, the legislation first establishes the minimum requirements that the site for storage of vehicles, including temporary storage, must have. In particular, it is about appropriate areas with impermeable surfaces, spillage collection facilities, decanters and cleanser-degreasers, equipment for the treatment of water including rainwater. In addition, the treatment sites must include adequate storage of dismantled spare parts, of batteries after electrolyte neutralisation, of filters and PCB/PCT-containing condensers. Components contaminated with oils must be stored on impermeable sites, while tire storage must include a fire protection system. All vehicle fluids such as fuel, motor oil, cooling liquid, antifreeze, air-conditioning system fluids and others must be stored separately in appropriate tanks. The removal of all these fluids is one of the operation necessary for the depollution of end-of-life vehicles. In addition, it is necessary to remove batteries, liquified gas tanks, potential explosive components such as air bags and all components identified as containing mercury. At this stage must be removed the recyclable part such as all the components containing copper, aluminium and magnesium, catalysts, tires, glasses, and large plastic components including bumpers, dashboard and fluid containers. All the operations described so far must be carried out as soon as possible and avoiding to contaminate the subsequent shredder waste and compromise the possibility of reuse, recovery and recycling. All establishments or companies that carry out the treatment operation must possess a permit issued by the competent authorities or must be registered with the latter. The derogation from the permit can only be applied following an annual inspection that certifies the type and quantity of waste to be treated, in addition to the technical requirements to be complied with and the safety measures to be taken.

- **Reuse and recovery**: the directive encourage Member States to adopt the measures necessary for the reuse of suitable components and the recovery of those that cannot be reused. In this article of the directive the objectives to be achieved are set. Whereas the directive dates back to 2000, the first objective states that no later than 1 January 2006 end-of-life vehicles must be reused and recovered for a minimum of 85% in weight and recycled for a minimum of 80% in weight. But it is the goal set for 2015 by the directive which represents a real challenge for all car manufacturers:

  "no later than 1 January 2015, for all end-of life vehicles, the reuse and recovery shall be increased to a minimum of 95% by an average weight per vehicle and year. Within the same time limit, the re-use and recycling shall be increased to a minimum of 85% by an average weight per vehicle and year"

  Therefore, only 5% in weight of the car may be destined for landfill, while everything else must be reused or recovered. Often recovery means energy recovery in waste-to-energy plants, but this is limited by legislation. In fact, only 15% of that initial 95% can be used for energy recovery, the remaining 85% must be reused or recycled.

In order to harmonize the directive on end-of-life vehicles with those concerning batteries and accumulators (2006/66/CE) and waste electrical and electronic equipment (2012/19/EU) the European Commission has adopted the Waste Legislative Package in the frame of the Circular Economy Package. The Waste Legislative Package introduces the Directive 2018/849 which modifies the three previous directives concerning waste in terms of reporting obligation for the Member States.

In fact, until 2018, every three years the member states had to write a report indicating the effective implementation of the directives relating to end-of-life vehicles and waste electrical and electronic equipment. Directive (EU) 2018/849 repeals this obligation by using the statistical data which Member States report annually to Eurostat.

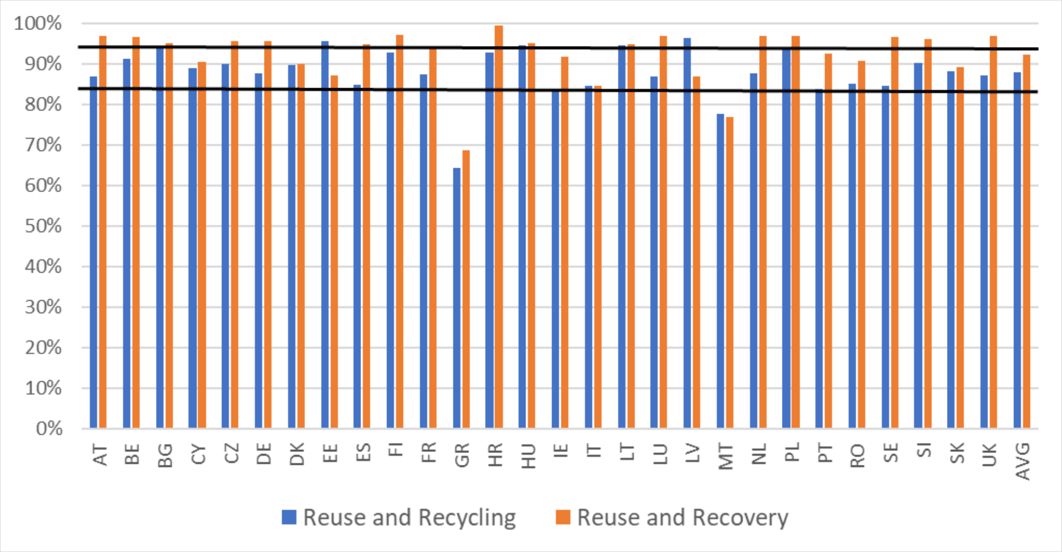


Figure 1.3 Reuse, recovery and recycling rates achieved by Member States in 2015. The black lines represent the objectives set at 95% for reuse and recovery and 85% for reuse and recycling [3].

The Figure 1.3 shows for each Member State of the European Union what percentage of reuse, recovery and recycling was achieved in 2015, the year in which the objectives, as indicated by the directive, rose to 95% for reuse and recovery and to 85% for reuse and recycling. It can be seen that 15 of the 28 Member States of the European Union had achieved both objectives. Other 8 states have achieved only one of the two targets with greater difficulty in reaching 95% of reuse and recovery. There are 5 states that in 2015 failed to achieve any of the two target set, namely Greece, Ireland, Italy, Malta and Portugal.

Therefore, Italy is one of the countries that failed to reach the targets set by the European Community. If we look in detail the trend of Italy from 2005 to 2016 in Figure 1.4, we can see that since 2007 there has been a significant improvement both in terms of recycling and recovery. Despite this, since 2007 it has continued to fluctuate around values of 83-84% without being able to improve the percentage in order to reach the targets. In fact, the target of 85% for recycling was only got closer in 2011 with 84.8% and then down again to the value of 82.5 in 2016. Even worse is what happened for the reuse and recovery, whose target of 95% was not reached at all with a maximum of 87.1% in 2008 down to 82.6% in 2016.

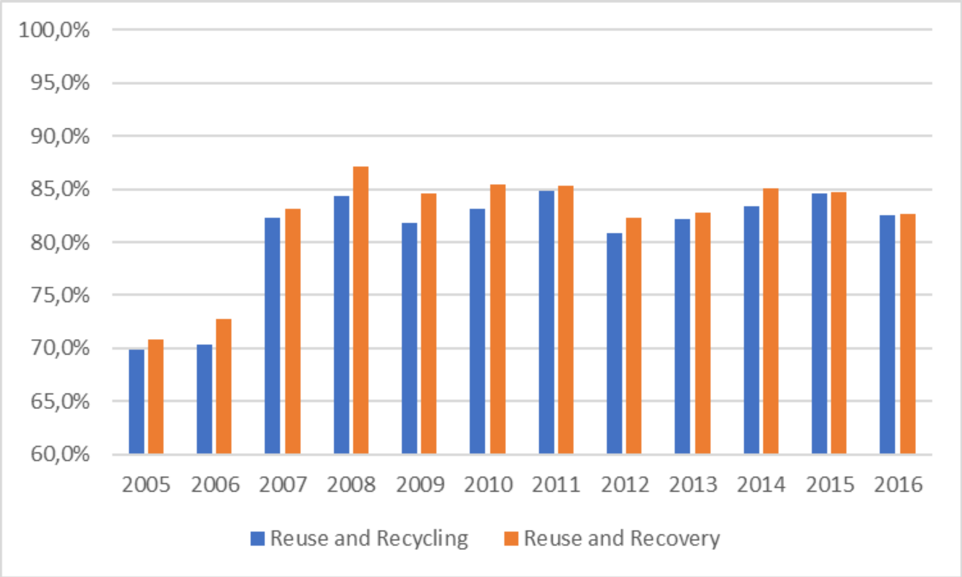


Figure 1.4 Reuse, recovery and recycling rates achieved by Italy from 2015 to 2016 [4]

Directive 2000/53/EC on end-of-life vehicles has been followed in directive 2005/64/EC on the type-approval of motor vehicles with regard to their reusability, recyclability and recoverability [5]. The latter provides that vehicles belonging to categories M_1 and N_1 can be put on the market only if recoverable to a minimum of 95% and recyclable to a minimum 85% by mass.

The categories M_1 e N_1 are defined in the Annex II of the directive 2001/116/EC [6] as follows:

- **Category M_1**: vehicles designed and constructed for the carriage of passengers and comprising no more than eight seats in addition to the driver's seat.
- **Category N_1**: vehicles designed and constructed for the carriage of goods and having a maximum mass not exceeding 3,5 tonnes.

Therefore, it is a responsibility of car manufacturers to verify the recoverability and recyclability of new vehicles in order to obtain type-approval. In detail the manufacturer must provide the nature of the materials used an all its component parts. These components must be attached to a list indicating how to perform the dismantling stage and the process that is recommended for their treatment. To obtain the vehicle type-approval, the manufacturer must first obtain a certificate of compliance from the competent body appointed by the Member States. The certificate of compliance is valid for two years and must be renewed before two years if significant changes have been made to the vehicle.

The directive also indicates all the components that cannot be reused in the construction of new vehicles. They are mainly safety components such as airbags, electronic control units and sensors, automatic or non-automatic seat belt assemblies and steering lock assemblies. Catalytic converter and particulate filters cannot also be used. All non-reusable components indicated by the directive must not be considered for the purposes of calculating the recyclability and recoverability rates.

1.3 Thematic strategy on waste prevention and recycling

The European Union's waste treatment policy aims to make waste a resource, in order to reduce the impact that waste has on the environment. The thematic strategy on waste prevention and recycling sets itself the long-term goal of making the European Union a society based on recycling and reducing waste production.

The strategy identifies seven fundamental actions aimed to achieving the set objectives.

1. **Implementation and enforcement of existing EU waste legislation**: in every legislative area it is not enough to issue laws, but to be effective it is necessary to guarantee their implementation. To this end, the European Union has increased its efforts to allow an effective implementation of waste legislation through the publication of documents that contain guidelines on the interpretation of laws. Despite this, it emerged that 19% of transfrontier shipments of waste occurred in violation of current legislation. Moreover, at the end of 2009, the waste accounted for 20% of all infringement proceedings concerning environmental law. For this reason, in many countries of the union it is not possible to achieve the objectives set with regard to environmental protection.
2. **Simplification and modernisation**: the simplification of legislation aims to reduce the cases of misinterpretation of regulations and make them more economically effective. For example the directives on waste electrical and electronic equipment (WEEE) [7] have been updated and rationalized to make them consistent with the most recent regulations [1,8,9]. It is estimated that this operation can reduce the administrative burdens regarding the registration obligations of WEEE up to 6 million euros. In addition, the new waste shipment regulation [10] has strengthened and simplified the procedures for controlling shipments through cooperation between Member States. Finally, the directives concerning hazardous waste and waste oils have been incorporated into the Waste framework directive and the requirements relating to national waste management plans have been simplified.

3. **Introducing life-cycle thinking in waste policy**: the concept of the life cycle takes into account the environmental impact over the entire life cycle of a product. The life cycle assessment approach follows all the steps “form the cradle to grave”, that means from the resource extraction (cradle) to the disposal phase (grave). The waste hierarchy puts prevention before reuse, recycling and recovery, relegating disposal as a last resort. However, Member States may deviate from the waste hierarchy if this is justified by the life cycle concept. The Eco-design Directive [11] applies the life cycle concept to the development of eco-design specifications for products in order to improve their environmental performance.
4. **Waste prevention**: the first step towards sustainable waste management is the prevention of waste production, as required by the waste hierarchy. To this end, the European Union is pushing for the introduction of national waste prevention programs that take into account examples of best practices from other Member States. Furthermore the regulations issued, such as Batteries Directive [12] and the Directive on the management of extractive waste [13], aim to prevent and limit the production of waste.
5. **Improving the knowledge base**: the management of complex problems such as waste can require access to a large amount of information and data. In fact, only on this basis the measures to be taken can be effectively decided. To this end, the European Commission cooperates with Eurostat, the European Environment Agency (EEA) and International Organisations. In particular Eurostat hosts a waste data centre which serves as a starting point for communications, reports and directives to be undertaken on waste.
6. **Development of recycling standards**: to guarantee the proper functioning of the internal market on recycling, the European Union has for more than twenty years been proposing various measures defining the minimum standards to be adopted by the Member Countries. These include the proposal for a directive on emissions from industrial plants, or the proposal for technical improvements available for the waste treatment industries [14].

7. **Further elaboration of the EU's recycling policy**: the internal recycling market has received a significant boost from a series of targets set by the waste regulations. These include those already discussed such as 85% for end-of-life cars, 50% for urban waste and 70% for construction and demolition waste. Lately the focus has shifted to organic waste. In fact, a study has been launched to further analyse the possibility of setting EU targets for the collection and recycling of organic waste.

Chapter 2

Polymer-based composite recycling

2.1 General recycling system

The recycling of composite materials like any other recycling operation requires a chain of operations in which each part is necessary for the next. Figure 2.1 illustrates the flow diagram showing the operations required for the entire recycling process [15–17].

Starting material can be of two types:

- End of life product
- Manufacturing scrap

The main difference between these two products is that end of life waste has undergone harder degradation processes than manufacturing scraps. It can be considered for example a composite laminate that undergoes a thermoforming process. We will obtain a component that will go into operation and waste material from the thermoforming process. The manufacturing scrap will have characteristics quite similar to the starting laminate, while the end of life component will have been subject to year of wear and degradation due to, depending on the application, thermal shock, chemical attacks, moisture, UV irradiation [18].

For both types of waste, it is necessary to have a collection and transport system (from the manufacturing industries for example) to the companies in charge of composite recycling. In the case of end-of-life waste these are assembled in manufactured products made up of many different types of components.

Consequently, it is necessary to disassemble the product and recover the composite part from it. At this point the composite material is recycled to obtain different types of recycled products that can be sold on the market.

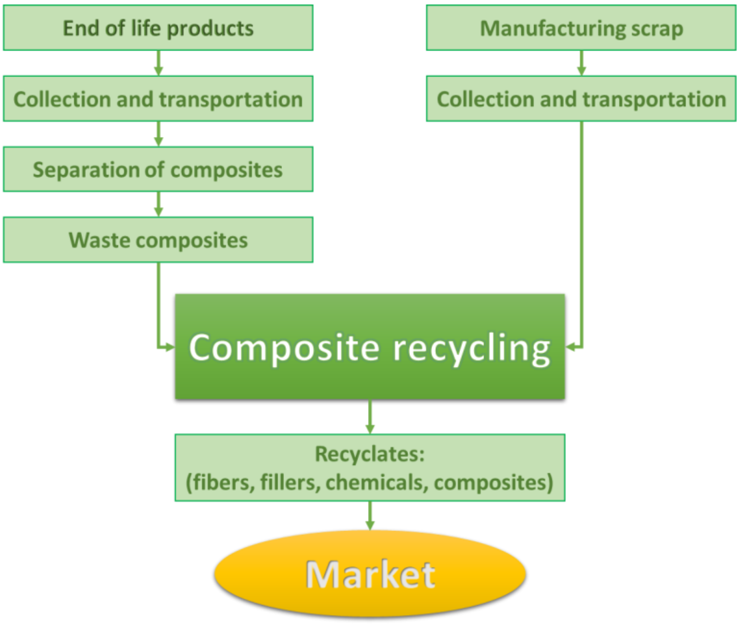


Figure 2.1 Flowchart of a generic composite material recycling system

The following paragraphs describe in detail all the recycling methods currently used for composite materials, summarized in Table 2.1.

Table 2.1 Current recycling operation for composite materials

Type of composites	**Recycling method**		**Kind of recovered goods**	**Status and drawbacks**
Thermoset matrix composite	Mechanical		Milled fibers	Industrially marketed
	Thermal	Pyrolysis	Fibers Oligomers	Industrially marketed
		Fluidised-bed		Only laboratory studies
	Chemical	Solvolysis	Fibers	Only laboratory studies
		Supercritical fluid	Fibers	Only laboratory studies
Thermoplastic matrix composites	Mechanical		Pellets	Mainly scraps treated. Mechanical properties degradation owing to fiber breakage

2.2 Recycling of thermosets matrix composites

2.2.1 Mechanical recycling

Mechanical recycling of composite materials provides for a first reduction in the size of scraps in the order of centimetres. This first operation is very useful both because it facilitates the removal of any metal inserts, and because from a logistic point of view it considerably reduces the volume of scraps for transport. This first size reduction can take place with a crushing mill or a band saw, while the main reduction is carried out by using an hammer mill or high speed mill, to obtain fraction ranging from millimetres to tens of microns [19].

In this way it is obtained a product containing all the constituents of the initial composite (matrix, fibers and fillers) in the form of granules. The ground material is classified according to the granulometry through system as cyclones or sieves [19,20]. Typically, the finest fraction has a higher polymer and filler content than the original composite, while the coarser fraction has a high fiber content. This last fraction appears to be more fibrous in appearance the higher the fiber aspect ratio of the initial composite is [19–21].

The problem of the mechanical recycling of thermosetting matrix composites is that the matrix cannot be reprocessed in temperature. Furthermore, if the starting composite is a laminate, the mechanical recycling leads to fiber breakage.

Therefore, until now the main applications of mechanical recycling of thermosetting matrix composites consists in their use as a filler. Bream et al. have used the products of mechanical recycling of thermosetting composites as a filler for thermoplastic materials. In particular, this is the case of a polyester matrix composite reinforced with 22% short glass fibers and a phenolic matrix laminate containing 80% of glass fibers. The addition of the ground materials in the formulation of a polypropylene component improved the mechanical properties by 50% thanks to the use of a compatibilizer between the different types of polymers [22].

As explained in paragraph 2.4, the industrial applications of mechanical recycling technique mainly concern glass fiber reinforced composites, as the high commercial value of carbon fibers suggests to prefer an effective recovery by thermal recycling of these fibers [19,20,23].

2.2.2 Thermal recycling

Thermal recycling of polymeric matrix composite materials can take place using different techniques. The technique most commonly used is pyrolysis, although some laboratory-scale techniques such as the fluidized bed process have been developed more recently.

It should be stressed that in literature we often talk about recycling even in the case of energy recovery operations. As explained in the section 1.1 on the waste hierarchy, energy recovery and recycling are two operations that are classified differently from the European Union directives.

Pyrolysis process

Pyrolysis is a process of thermal decomposition of polymeric materials that takes place by heating them in the absence of oxygen. The heat supplied is not used to support the combustion of the material, but to break the chemical bonds of the polymer with the formation of smaller molecules [24,25].

A simplified diagram of a pyrolysis process is shown in Figure 2.2, where the developed hot gases are used to support reactor heating. The operation diagram of the process varies considerably depending on the type of pyrolysis which gives rise to different percentage of solid, liquid and gas products [26]. In the case of thermal depolymerization, as products of the process we will have on one side mainly monomers and oligomers and on the other side solid residues. In the case of composite materials the solid residue consists of fibers, fillers and char.

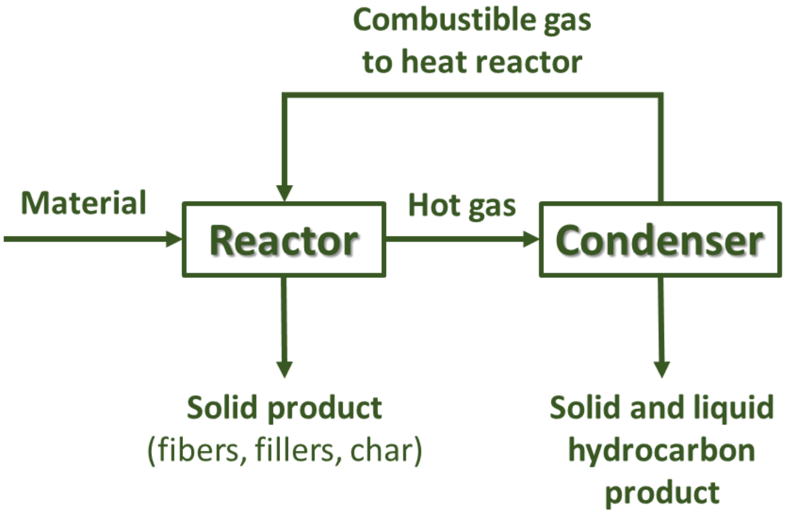


Figure 2.2 Scheme of pyrolysis process

At the beginning of the 90s the Automotive Alliance had developed a process of pyrolysis of car waste at temperatures between 700 and 1000 °C able to produce 70% of solid residue and oil and 30% of gas [27]. The solid residue, consisting of glass fibers, fillers and char, was then ground and reused as a filler for other car components. The use of high temperatures for pyrolysis leads to damaging of glass fibers, consequently, since the 90s processes at lower temperatures have been investigated [28]. Soh et al used a temperature of 400°C in the presence of steam in order to easily recover and separate the glass fibers. These rescued fibers, after being cleaned from the remaining residue, were mechanically testes maintaining 50% of their specific fracture energy.

A more structured work on the pyrolysis of polymer composites was conducted by Cunliffe et al [26]. They pyrolyzed at temperatures between 350 and 800°C different thermoplastic and thermosetting resins reinforced with glass or carbon fibers. Table 2.2 shows the solid products obtained, expressed as percentage in weight of the different types of composites in relation to pyrolysis temperature. It can be seen that for composites with polyester, phenolic and epoxy matrix, as the pyrolysis temperature increases, the percentage of solid residue decreases. This causes an increase in liquid and gaseous products. If the products are compared at the temperature between 500 and 550°C for the various composites it can be seen how the yield of the solid fraction is strongly dependent on the type of polymeric matrix. For the polyester matrix composite fibers were recovered. Tensile tests on these fibers have shown that tensile strength measured up to 650°C maintains 50% of the value of virgin fibers and then it decreases to 18% passing to 800°C.

Table 2.2 Product yields from the pyrolysis of various composites in relation to final pyrolysis temperature [26].

Composite	Temperature [°C]	Solid Residue [wt.%]	Oil/Wax [wt.%]	Gas [wt.%]
Polyester resin with calcium carbonate, alumina trihydrate fillers and glass fibers	350	82.9	14.5	2.6
	400	52.6	41.2	6.2
	450	48.7	45.0	6.3
	500	45.8	45.7	8.5
	650	46.6	47.0	6.4
	800	38.2	67.4	14.4
Phenolic resin (24 wt.%) with magnesium oxide and calcium carbonate fillers, glass fibers reinforcement	400	94.3	5.1	0.6
	500	90.2	8.8	1.0
	600	86.6	10.9	2.6
	700	85.3	12.0	2.8
	800	83.4	11.9	4.6
Epoxy resin with glass and carbon fibers reinforcement	350	81.7	18.0	0.2
	400	70.7	27.6	1.7
	500	67.4	31.3	1.2
	600	69.6	29.4	1.0
	800	65.3	31.7	3.0
Polyester resin (70-80 wt.%), glass fibers, silane binder	550	30.0	59.4	10.6
Polypropylene resin (60 wt.%), glass fibers, silane binder	550	44.8	46.8	8.4
Polyethylene terephthalate resin (50 wt.%) with glass fibers	550	74.4	13.0	12.6
Vinylester resin (30 wt.%) with woven glass fibers fabric	550	83.4	15.0	1.6

Therefore, at the end of a pyrolysis the solid fraction is the one with the highest percentage between 50-70%, followed by liquid products (10-50%) and gaseous fraction (5-15%).

The fibers recovered after pyrolysis have mechanical properties that are often too poor to be used in composite formulations. For this reason a regeneration treatment of fiber strength has been recently proposed by Thomason et al [29]. Using hot sodium hydroxide solution, the recovered fibers can increase their strength more than three times. Furthermore, adding to the sodium hydroxide treatment a silane-based coupling agent the mechanical properties further improve.

Fluidised-bed thermal process

The method of recovering glass and carbon fibers from composite scraps using a fluidized bed process was developed at Nottingham University at the beginning of this century [30]. The bed is made of silica sand with a size of about 0.85 mm and fluidized with a stream of hot air at 450-550 °C and 0.4-1.0 m/s.

A model of the process is outlined in the Figure 2.3. The air flow is heated passing around some preheating elements. The presence of an oxidizing atmosphere allows the char, formed by thermal decomposition of the polymer, to oxidize leaving clean fibers. The composite scraps are reduced in size to about 25 mm and then are inserted through a side entrance towards the fluidized bed. In the fluidized bed the hot steam causes the volatilization of polymeric matrix, leaving the fibers free and suspended as single particles in the gas steam. In a cyclone the separation between the fibers and the exhaust gas occurs. In a secondary combustion chamber the gas steam is heated at high temperature to completely oxidize the remaining polymer volatiles.

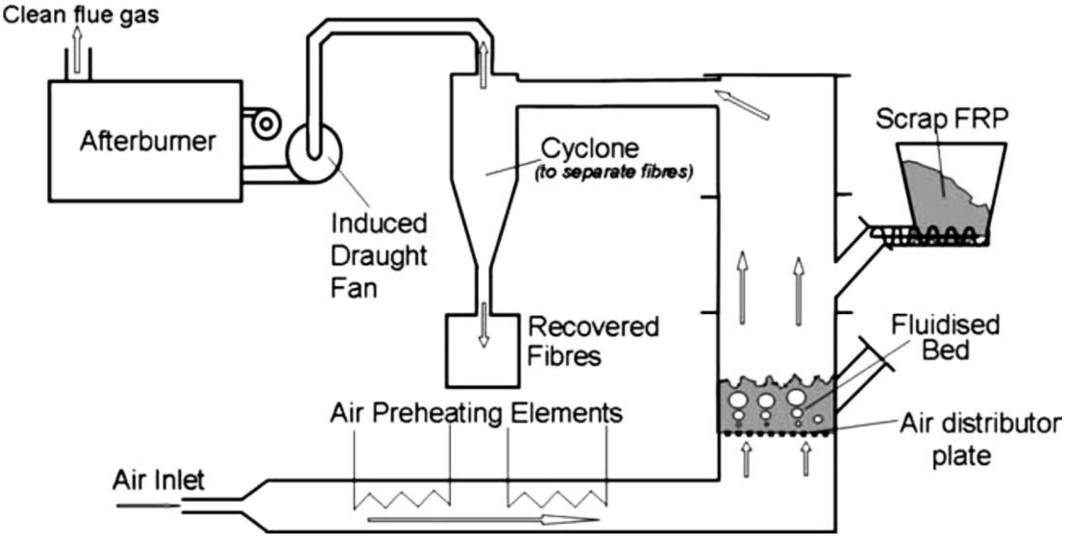


Figure 2.3 Scheme of fluidised bed thermal process

The fibers collected by the fluid bed process typically are discontinuous, very fluffy and highly entangled, with a length in the order of some millimeters.

The diagram shown in Figure 2.3 represents the laboratory-scale process. Recently, the University of Nottingham has also upgraded the system to a scale representative of a commercial operation [31,32]. The characterization of the carbon fibers recovered from composite scraps waste were different for the two fluid bed systems. The results from the fluidized bed on a laboratory scale showed a Young modulus similar to virgin carbon fibers, but a reduction between 25-50% of the strength. In the case of the most advanced system, there was an 18% decrease in tensile strength. This is an encouraging result that justifies the scaled up of the system.

An advantage of the fluidized bed system is that it is very flexible and tolerant towards mixed and contaminated materials. In fact, it can process mixtures of composites, composites made of sandwich structures and painted composites. Any metal inserts must not be removed before the process, because the metal remains in the sand bed and can be removed later.

2.2.3 Chemical recycling

The chemical recycling of composite materials consists in dissolving the matrix by depolymerization or other chemical process in order to recover the fibers and other fillers. In the case of depolymerization it is also possible to recover the constituent substances of the matrix in the form of monomers and oligomer.

Low temperature solvolysis

Depending on the type of solvent used, the matrix dissolution process, often called **solvolysis**, is defined as follows:

- **Hydrolysis**: if the solvent used is water
- **Glycolysis**: if the solvent used is glycols
- **Acid digestion**: if the solvent used is an acid

The literature shows that considerable efforts have been made to try to recover the reinforced epoxy composites chemically.

In Wang et al. work chemical recycling is carried out by acid digestion with a degradation system made of $AlCl_3/CH_3COOH$ that allows for selective cleavage of the Carbon-Nitrogen bond [33]. Using this method 97% of the fibers is recovered, while maintaining nearly unchanged their mechanical properties compared to that of virgin carbon fibers.

Another work by Yamaguchi et al. showed how carbon fibers can be recovered from epoxy matrix composites containing degradable acetal linkage. The chemical recovery of the fibers takes place with a hydrochloric acid in tetrahydrofuran treatment that preserves the tensile properties [34]. Another strategy proposed by Li et al. involves the recovery of carbon fibers by immerging the epoxy composite in a solution of acetone and hydrogen peroxide at 60°C for 30 minutes. In this way there is a decomposition of 90% of the matrix and the remaining fibers show 95% of the tensile strength of the virgin ones [35].

From what can be seen in the literature most of the works regarding the chemical recycling of thermosetting composites concern the recovery of carbon fibers with high commercial value. Less interest is placed towards the matrix which is dissolved through the solvolysis processes. Despite this, some attempts have been made to recover the solvolysis reaction products. In a recent work it was shown that it is possible to use the oligomers coming from the decomposition of the epoxy matrix as reagents to prepare new epoxy resin. The new epoxy system maintains the mechanical strength properties if the system contains up to 15% recycled resin. For values over 15% the flexural strength values drop over 50% compared to 100% virgin resin [36].

In the automotive sector in the 80s, General Motors patented a method for recovering polyurethane foams. Through hydrolysis it was possible to recover diamines, polyol and carbon dioxide under high pressure and temperature [37].

Supercritical fluids

Another approach to chemical recycling involves the use of supercritical fluids. A fluid is defined at the supercritical state when it is above both critical pressure and critical temperature [38]. Under these conditions it is not possible to distinguish whether the material is liquid or gaseous. In fact, a supercritical fluid preserves the low viscosity of the gas and the high density of the liquid.

The use of supercritical fluids allows the depolymerization or decomposition of polymeric materials rapidly compared to the usual chemical techniques [39]. In particular, water and alcohol are used in supercritical conditions.

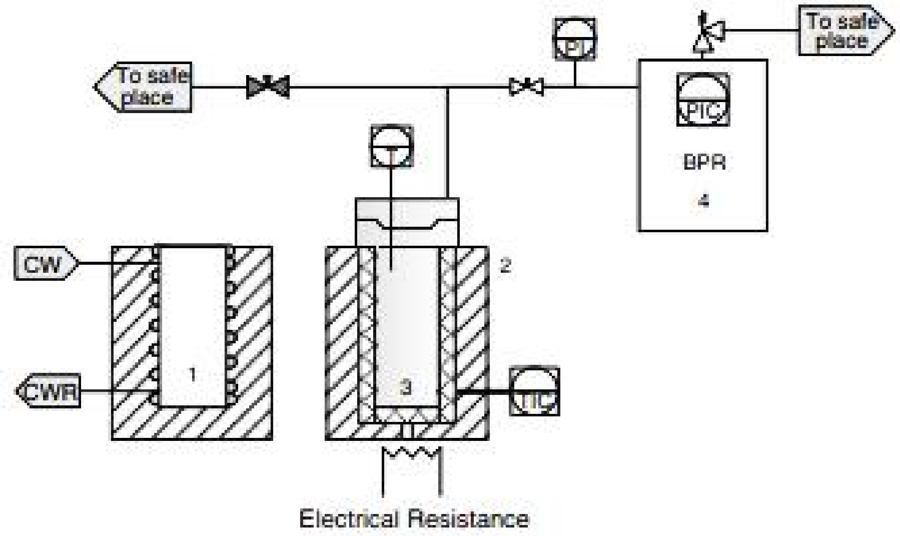


Figure 2.4 Scheme of chemical recycling using supercritical fluids: (1) cooling block, (2) heating block, (3) autoclave, (4) back pressure regulator.

The figure 2.4 shows a typical system adopted for the recycling of composites using supercritical fluids. The system consists of a 10 ml stainless-steel autoclave in which the composite material is positioned. First, the autoclave is placed in an aluminium heating block connected to an electrical resistance and to a pressure regulations system. Another cooling block is used to quench the reaction after each experiment. The system does not provide mechanical agitation to avoid fibers damaging.

The work of Piñero-Hernanz et al. has shown that by using supercritical water conditions (29 MPa and 673K) is possible to achieve a yield of almost 80% without the use of catalysts in the recovering of carbon fibers from epoxy resin. Differently, using catalytic alkaline species such as KOH allows the elimination of 95.4% of the resin with tensile strength close to virgin fibers [40]. Using alcoholic substances in supercritical conditions, such as methanol, ethanol and propanol, it is even possible to recover more than 95% of carbon fibers in the absence of catalysts [41]. Table 2.3 summarizes the chemical recycling conditions used in different studies on epoxy/carbon fiber composites in terms of solvent used with or without catalyst, time, pressure, temperature and yield of the dissolution reaction.

Table 2.3 Chemical recycling conditions in the literature of epoxy/carbon fibers composites by using supercritical fluid

	Solvent	**Time [min]**	**Pressure [MPa]**	**Temp. [°C]**	**Catalyst**	**Yield [%]**
Okajima et al. [42]	Water	-	25	380	No	90
Piñero-Hernanz et al. [40]	Water	30	29	400	No	79.3
					Yes	95.4
Bai et al. [43]	Water	30	30	440	No	95
Jiang et al. [44]	n-Propanol	20	5.2	310	No	-
Piñero-Hernanz et al. [41]	Alcohols	70	15	350	No	96.5
				275	Yes	98

Although by using supercritical fluids it is possible to effectively recover carbon fibers, to date the system used remains on a laboratory scale. Moreover, the higher yields are obtained through the use of catalytic substances, which hardly can be separated from the degradation reaction products.

2.3 Recycling of thermoplastic matrix composites

Thermoplastic matrix composites currently occupy a secondary sector in the composites market compared to those with a thermosetting matrix [45]. This is mainly due to some advantages of thermosetting composites. In fact, they guarantee better mechanical properties, resistance to temperatures and durability [46].

Therefore, the greater use of thermosetting matrix composites has consequently led to a strong push in the study of the recycling method of these materials as shown in the previous paragraphs. As a consequence, less effort has been undertaken in the study of recycling techniques for thermoplastic composite materials.

Nevertheless, the characteristic of the thermoplastic matrices of being able to be reformed once heated, places them favourably as regards the possibilities of recycling. In fact, due to this characteristic, thermoplastic composites are mainly recycled by remelting and remoulding directly the material [47,48].

In the case of thermoplastic composites, investigations were carried out using a mechanical recycling technique. Among the first attempts on mechanical recycling of carbon-fiber reinforced thermoplastic composites there is the study conducted by Schinner et al. Here the possibilities of recycling a carbon fiber reinforced PEEK matrix composite were investigated through two different approaches. The first involves grinding the composite to use the ground fraction to reinforce virgin PEEK in injection moulding or compression moulding compounds. The second approach consists in remoulding in temperature the product obtained in order to minimize the production waste. The products thus obtained have lower mechanical properties than the starting laminate but greater than similar injection moulding compounds [49].

Otheguy et al. have studied the possibility of recycling an end-of-life hull of a boat constituted by a polypropylene laminate containing 60% by weight of glass fibers along with balsa core material. Mechanical recycling was carried out by reducing the dimensions of the laminates with a pneumatic saw into about 15 mm squares. Since 60% of glass fiber is a too high percentage to forming the material by injection moulding, it has been compounded into an extruder with virgin polypropylene to reduce the amount of fiber. The granulate thus obtained was injection moulded to obtain tensile test specimens. The mechanical tensile properties achieved showed a strength in the order of 100 MPa and a modulus greater than 8 GPa. These are values that fall within the range of commercial interest, especially in automotive applications that already use polypropylene reinforced with talc or glass fibers [50].

Although it is interesting to understand the recycling behaviour of a component at the end of its life, most of the studies carried out so far in the literature concern the recycling of the thermoplastic material intended as its reprocessing. For example, the properties after mechanical recycling of a 40% glass fiber reinforced polypropylene composite were analysed in a work by Colucci et al. [51]. The injection moulded composite was shredded and re-processed obtaining two other products, one with 50% recycled material and another with 100%. Table 2.4 shows the results obtained in terms of mechanical properties of recycled products compared to the virgin one. It can be seen how using the recycled composite there is a 13% decrease in both Young modulus and tensile strength, while the deformation remains almost the same. Despite this, the mechanical properties of recycled products remain on values that are still commercially valid.

Table 2.4 Tensile properties of polypropylene matrix containing 40 wt.% of glass fibers with different percentage of recycled material [51]

Sample	Young modulus [GPa]	Strength [MPa]	Strain at break [%]
Pristine PP40GFs	9.4 ± 0.5	112.3 ± 2.3	2.0 ± 0.1
50% Recycled PP40GFs	8.2 ± 0.5	96.9 ± 1.1	2.1 ± 0.1
100% Recycled PP40GFs	8.6 ± 0.2	85.6 ± 0.7	2.2 ± 0.1

Other studies have been carried out on the recycling of polyamides reinforced with both carbon and glass fibers. Always concerning glass fibers a work similar to the previous one was carried out by Bernasconi et al [52]. In this case it is a polyamide 6,6 reinforced with 35% of glass fibers that has been grounded and reinjection moulded with virgin material with different percentages of recycled material. From the results about the mechanical properties shown in the table 2.5 it can be seen that the use of composites obtained with partly recycled material determines a satisfactory maintenance of the mechanical properties in terms of modulus and strength. The 100% recycled sample shows a 11% decrease in strength and 5% in modulus, remaining however at satisfactory value.

Table 2.5 Tensile properties of polyamide 6,6 matrix containing 35wt.% of glass fibers with different percentage of recycled material [52]

Sample	Young modulus [GPa]	Strength [MPa]	Strain at break [%]
Pristine PA66+35GFs	10.84 ± 0.14	187.9 ± 2.4	2.87 ± 0.13
25% Recycled PA66+35GFs	10.75 ± 0.13	185.9 ± 0.5	2.85 ± 0.06
50% Recycled PA66+35GFs	10.73 ± 0.09	181.6 ± 0.7	3.00 ± 0.06
100% Recycled PA66+35GFs	10.27 ± 0.12	167.3 ± 1.6	3.04 ± 0.09

The two works just discussed dealt with understanding the behaviour of the composite material after milling and reforming to obtain products with variable percentages of recycled material. Although this kind of investigations are interesting to understand the technological possibilities of printing non-virgin thermoplastic composites, these materials have not undergone natural aging. In fact, a component in operation may be subject to degradation due to mechanical stress, changes in temperature, humidity or atmospheric natural agents. To take account of these factors, some studies on the recycling of composite materials simulate degradation by artificial aging. In another work of Colucci et al. this has occurred using an accelerated weathering tester that reproduces outdoor moisture and the degradation effect of sun rays through a fluorescent UV radiation [53]. Comparing the resistance values reported in table 2.6 between the pristine and recycled polyamide 6,6 reinforced with 30% of carbon fibers, it can be seen how there is a 20% drop in tensile strength. This value is well above that of the 12% obtained in the previous work, which did not take into consideration the aging of the material. In particular, artificial aging has led to a 14% decrease in the module and 16% in resistance.

Table 2.6 Tensile properties of pristine, aged and recycled polyamide 6,6 matrix containing 30wt.% of carbon fibers [53]

Sample	Young modulus [GPa]	Strength [MPa]	Strain at break [%]
Pristine PA66+30CFs	23.5 ± 0.6	236.4 ± 3.8	1.7 ± 0.1
Aged PA66+30CFs	20.2 ± 0.2	198.5 ± 4.6	2.0 ± 0.1
Recycled PA66+30CFs	20.5 ± 0.7	188.2 ± 1.3	1.7 ± 0.1

As seen before, the mechanical recycling of composites requires, first of all, the grinding of the material which can take place with different machines. The choice of the type of grinding affects the final length distribution of the fibers. For example the use of a cutting mill leads to a more homogeneous fiber-length distribution than an hammer mill [49]. The loss of performance of the composite material subjected to mechanical recycling is mainly associated with the breakage of the fibers caused by the grinding operations.

2.4 Recycling composites commercially

Although there are various techniques for recycling fiber reinforced composite materials, to date the number of companies that can recycle on a large scale is less than 10 worldwide. Starting from laboratory research in collaboration with universities, there have been many attempts by companies to find commercially remunerative ways of recycling composite materials.

Most of the efforts involved carbon fiber-reinforced composites since these have a commercial value of an order of magnitude higher than glass fibers. This was possible also thanks to the push of the aerospace and transport industries that strongly use carbon fiber composites. The high cost of carbon fibers has made it possible to create a market for recycled carbon fibers at a competitive price compared to virgin one.

The recovery of carbon fibers occurs in most cases through the thermal pyrolysis process of the plastic matrix. Composite manufacture waste or carbon fiber end-of-life components are therefore processed to recover their fibers and turn them into new commercial products. These products differ according to the length of the fibers that ranges from the fraction of a millimetre up to few centimetres. In fact, chopped and milled fibers [54–57], non-woven mats [55,56] and preforms [55] can be found on the market.

Another commercially undertaken route concerns the mechanical recycling of fiber reinforced thermosetting composites. The pioneers of this possibility were companies like ERCOM in Germany and Phoenix Fibreglass in Canada in the early 1990s [19,21]. These two companies were the first to develop a mechanical recycling process of fiber-reinforced thermosetting composites on an industrial scale. Since they started production when there was no real market for recycled composite materials, both companies terminated production for economic problem more than twenty years ago.

In the case of mechanical recycling of thermosetting matrix composites most commercial applications concern composites reinforced with glass fibers [19,20,23]. In fact, since glass fibers have a low economic value, their use as a filler can be justified. The main applications of this type of recycled material concern the building, railway and road industries [20,58–60].

Finally, as regards the chemical recycling of fiber reinforced composites, the existing works have been developed on a laboratory scale or on pilot plants. Some companies like Adherent Technologies have developed pilot plants capable of processing tens of kilograms of material by solvolysis. At present their purpose is to sell or license the technology [61].

Table 2.7 summarizes the companies that recycle fiber-reinforced polymer composites. It can be seen how these are located almost exclusively in North America or Europe. And it is precisely for the strong restrictions in force in Europe in terms of recycling, that in recent years a market for recycled composite products has been born.

Below there is a list of companies that are currently involved, with the exception of the first two, in recycling of polymer based composite materials:

- **Phoenix Fibreglass Inc**: it was a Canadian company from Ontario that was the first to implement mechanical recycling of thermosetting fiberglass composites at an industrial level. Starting from composites they get three different typed of composite products based on the grain size of the ground [19]. Furthermore, a fourth product consist of the recovery of single short glass fibers. Therefore the Phoenix Fibreglass was able to separate part of the fibers from the starting composites through a process patented by the company itself [62].
- **ERCOM Composite Recycling GmbH**: it was a German company that mechanically recycled composite waste in a plant with a capacity of 4000 tons a year. The ground was classified into three powder products depending on the grain size and three fiber products depending on the average fiber length. As the length of the fibers increased, the value of the product as a reinforcement and therefore the price on the market increased [21].
- **Mixt Composites Recyclables (MCR)**: is a French company specialized in the manufacture of thermosetting compounds such as Sheet Moulding, Bulk Moulding and Advanced Moulding Compound in automotive, electrical and railways industries. They use mechanical recycling of composites to obtain products to be used as fillers in paving concrete and asphalt road [58].

- **Fiberline Composites**: is a Danish company producing composite materials for structural applications. The company has drawn up a contract with the Swiss cement manufacturer to use its glass fibers as a filler in cement. The glass fiber treatment process is carried out in another company located in Germany that deals with mechanical recycling [59].
- **Eco-Wolf Inc**: is an American company based in Florida that produces systems for mechanical recycling of fiber reinforced plastic composed of a grinder and a dispensing macerator. In this way they recover fibers with dimensions from 2.5 mm to fine powders [63].
- **Hambleside Danelaw**: is an English company that has developed a process of mechanical recycling of glass fibers in thermosetting matrices. The fibers are used as a reinforcement or individually or to form a non-woven fabric. The main application of these materials relates to uses in the building sector [23].
- **Reprocover**: is a Belgian company that manufactures products for the railway and road industry made of reprocessed thermosetting materials. Everything is done by mechanical recycling followed by compacting using a high-pressure press [60].
- **Global fiberglass solutions**: is an English company that mechanically recycles glass fiber reinforced thermosetting composites. Waste fiberglass becomes feedstock for a series of application from railway to building product [20].
- **ELG Carbon Fibre Ltd**: is an English company that has developed the world's first and largest carbon fiber recovery line, with a plant with a capacity of 2000 tonnes/years. The process concerns the chemical recover by pyrolysis of carbon fibers from scrap prepreg materials or cured laminates. These products can come either from manufacturing waste or from real end-of-life components. The recovered fibers are then used in the automotive, aerospace and railway industries [64].
- **CFK Valley Stade Recycling**: is an English company that deals with recovering of production scraps or end-of-life components in carbon fiber reinforced composite material. The process involves the initial crushing and selection of the material according to the type of starting product, the subsequent heat treatment of pyrolysis and the finishing of the obtained

fibers. Finally there is the cutting of the fibers to obtain the "chopped" commercial products with different lengths of fiber available and "milled" useful for the dispersion in different materials [54].

- **Carbon conversions**: is an American company based in South Carolina that recycles all types of waste in carbon fiber-reinforced plastic recovering its fibers through a pyrolysis process. The company sells short length fibers in the 0.5-2.5 mm range through three commercial products that differ in mechanical properties. It also produces non-woven mats using 100% recycled carbon fiber or a mixture of carbon fibers and thermoplastic fibers. Finally they also produce three-dimensional preforms in carbon fiber suitable for the realization of complex components [55].
- **Karborek RCF**: is an Italian company that recovers manufacturing waste and end-of-life materials containing carbon fibers and then takes care of the fibers recovery and putting them on the market. The process involves thermal recycling by pyrolysis of the composites in a 1500 tonnes/year plant. The recovered carbon fibers are then marketed in the form of two products, one consisting of short carbon fibers and the other of a carbon fiber felt [56].
- **Hadeg Recycling Ltd**: is a German company founded in 1995 that recycles carbon fibers recovering them from composite component waste by pyrolysis process. From prepreg remnants they produce a whole series of products including carbon fibers reinforcing plastic component, carbon short fibers, cut fibers and milled fibers based on the length of the fibers [57].
- **Adherent Technologies Inc**: is a US company based in New Mexico that offers composite related technologies such as reactive fiber finishes and composite repair primers. In parallel it has developed in a pilot plant a technology for the chemical recovery of carbon fibers from reinforced composite material. The process is based on the chemical degradation of the polymeric matrix followed by the separation of the fibers from the liquid products by centrifugation. The process leads to the production of short carbon fibers variable in length from the fraction of a millimetre to the 5 cm that maintain 95% of the resistance of the virgin fibers [61].

Table 2.7 Companies involved in the recycling of polymer-based composites

Company	Location	Recycling method	Material recycled
Phoenix Fibreglass Inc	Canada	Mechanical	GFRP waste
ERCOM Composite Recycling	Germany	Mechanical	FRP waste
Mixt Composites Recyclables	France	Mechanical	Thermoset compounds
Fiberline Composites	Denmark	Mechanical	FRP scraps
Eco-Wolf	United States	Mechanical	FRP composite
Hambleside Danelaw	United Kingdom	Mechanical	Thermoset GFRP
Reprocover	Belgium	Mechanical	Thermoset GFRP
Global fiberglass solutions	United Kingdom	Mechanical	Thermoset GFRP
ELG Carbon Fibre	United Kingdom	Pyrolysis	Scraps and end-of-life CFRP
CFK Valley Stade Recycling	United Kingdom	Pyrolysis	Scraps and end-of-life CFRP
Carbon Conversions	United States	Pyrolysis	Scraps and end-of-life CFRP
Karborek RCF	Italy	Pyrolysis	CFRP scraps
Hadeg Recycling Ltd	Germany	Pyrolysis	CFRP remnants
Adherent Technologies Inc	United States	Chemical	CFRP composites

Chapter 3

Glass-fiber reinforced polyamide matrix composites

In this chapter the properties of polymer matrix composites reinforced with glass fibers are reported. In the first two paragraphs matrix and reinforcing phase are analysed separately, while in the third paragraph the mechanical properties of composites reinforce with short fibers are investigated.

3.1 Polyamide matrix

Polymeric materials can be classified in different ways depending on the synthesis process, the structure, the thermal behaviour and the presence of groups that confer certain properties.

The last category includes Polyamides (PA), a class of polymers characterized by the presence of the amide group -NHCO-, shown in Figure 3.1, typically obtained by reaction between a carboxylic acid and an amine [65].

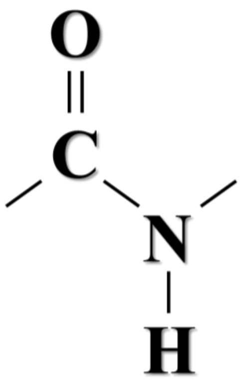


Figure 3.1 Representation of the chemical bonds of the amide group

The historical origin of polyamides dates back to the beginning of the twentieth century when by heating a carboxylic acid and caprolactam von Braun hypothesized obtaining an amide polymer. But it was only in the 1930s that Carothers, at the Du Pont research laboratories in the United States, undertook extensive experimentation with polyamides. Until in 1935 the first patent was issued for the synthesis of polyamide 6,6 with the commercial name of Nylon [66]. The production of nylon began in 1939 and was used during the Second World War in the form of a filament to produce high tenacity ropes and make parachutes. Starting from those years the production of nylon fibers has grown to over 5,000 tons in recent years (Figure 3.2) [67].

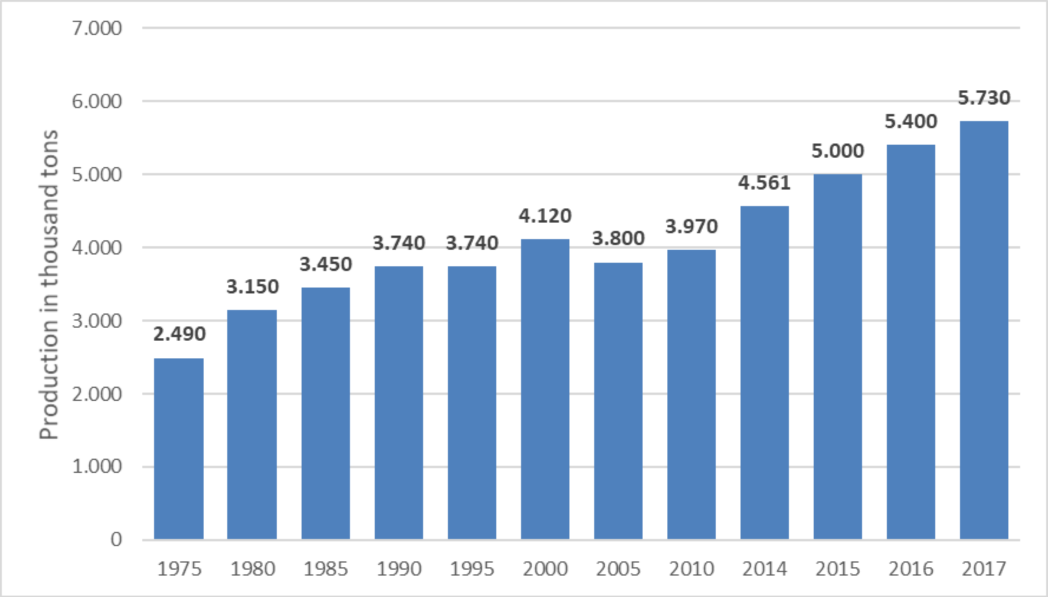


Figure 3.2 Production of polyamide fibers worldwide from 1975 to 2017

To date, almost all of the world's polyamide production concerns PA6 and PA66, of which 70% is in fiber form [68]. Although the market is saturated with only two polyamides, there are many types. In the Carothers patents are already described examples for the preparation of PA 3,10; 5,18; 5,10; e 2,18.

The difference between the various types of polyamide is in the synthesis method and in the length of the aliphatic chains interposed between the amide groups. The nomenclature of the polyamides is based on the monomers from which they are synthesized, that is if the group amino (A) and carboxylic (B) are on two monomers or one; and from how many carbon atoms (n) are made the monomers. It is possible to distinguish polyamides in two types:

1. **PA n** or **A-B type**: are the polyamides obtained from ω-aminoacid monomers that contain both the amino and carboxylic group. For this type of polyamides, groups A and B are repeated at intervals from the aliphatic part according to a pattern of the type:

   A-BA-BA-BA….B

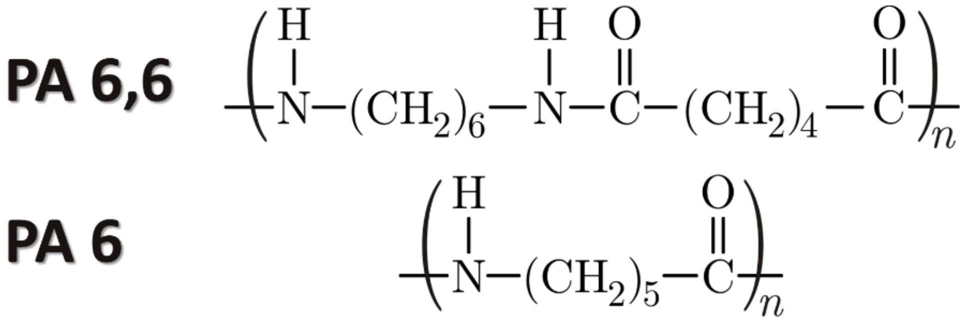
   Polyamides of this type are identified by putting the number of carbon atoms *n* after the abbreviation PA

2. **PA n,n** or **A-A, B-B type**: are the polyamides obtained by polymerization of a diamine A-A with a diacid B-B. In this case the general structure of the polymer is:

   A-AB-BA-AB-BA-AB-B….B-B

   To identify them two numbers *n,n* are used, the first represents the number of the carbon atoms of the diamine and the second those of the diacid.

The structures of the most used polyamides PA6 and PA66 are reported in the Figure 3.3. PA66 is obtained by polycondensation between hexamethylenediamine and adipic acid, while PA6 is synthesized by ring-opening polymerization of caprolactam.



PA 6,6

$$\left(\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_6-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}} \right)_n$$

PA 6

$$\left(\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}} \right)_n$$

Figure 3.3 Structural formula of polyamide 6 and polyamide 6,6

Polyamides are industrially interesting because, despite being thermoplastic polymers, they have excellent mechanical properties, which allow them to be classified as technopolymers. To understand the reasons that guarantee the performance of polyamides, we need to analyse their structure. Polyamides are thermoplastic materials with a semi-crystalline structure, whose degree of crystallinity depends on the quantity of polar amidic groups responsible for the formation of hydrogen bonds, which guarantee high cohesive energy between the chains. The crystalline part consists of regions in which portions of macromolecule are arranged in an orderly manner and parallel to each other to form lamellae. The lamellae are arranged in spherical aggregates called spherulites [69].

Therefore, the crystalline structure of the polyamides is determined by the possibility of the amide group to establish intermolecular hydrogen bonds with carboxylic groups. The chains are arranged to maximize this type of bonds that stabilize the structure. In fact, the hydrogen bonds are able to order the polyamide macromolecule in exceptionally strong planar layers.

The disposition of the macromolecules, induced by the hydrogen bonds during the crystallization, determines the crystalline structures of the polyamides, which therefore are characterized by polymorphism.

The two stable forms of polyamides are the α and γ. The α-form, shown in the Figure 3.4 for PA66, has triclinic crystalline symmetry, with only one molecular unit per cell unit. The macromolecules are linked together by hydrogen bridges that lie on the a-c planes of the cell. The cell parameters of α-PA66 are; a=0,49 nm; b=0,54 nm; c=1,72 nm; α=48,5°; β=77°; γ=63,5°. Instead, the γ form has a normally monoclinic crystal structure with β=121° that makes it pseudo-hexagonal. The cell parameters of γ -PA6 are; a=0,93 nm; b=1.688 nm; c=0,478 nm; α=90°; β=121°; γ=90°[70].

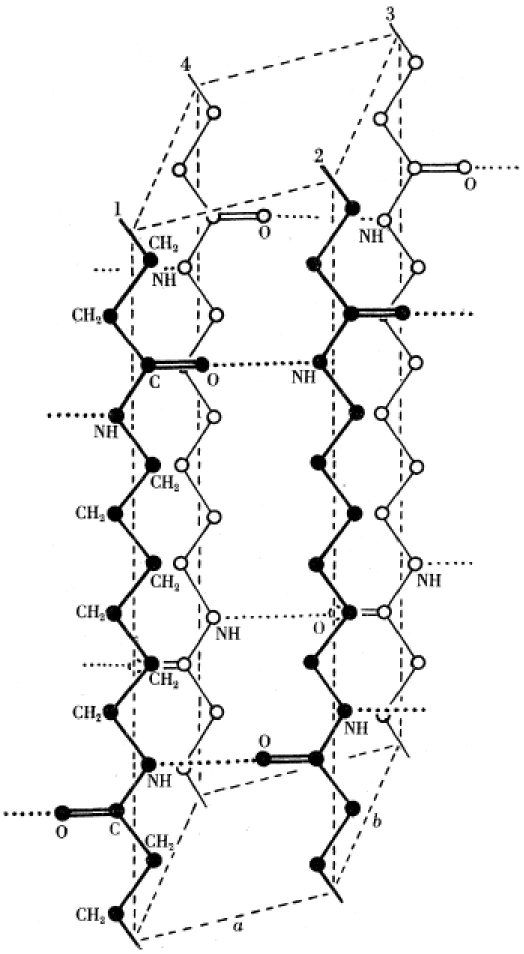


Figure 3.4 Structure of α crystal of polyamide 6,6 [70]

A variable ratio between α and γ phases is obtained according to the heating and cooling conditions of the samples. The α phase formation is hindered when the temperature and the crystallization time are increased [71].

Table 3.1 shows some properties regarding polyamides 6 and 6,6. The density is around values slightly above 1 g/cm^3. The main difference concerns the melting temperature, which is higher for polyamide 6,6. This makes PA66 more suitable for application where resistance to high temperature is required. The mechanical properties are expressed in a range of values since, being the polyamides semi-crystalline, their behaviour is a function of the degree of crystallinity. Polyamide 6,6 has higher modulus and strength values than the PA6 and consequentially lower elongation at break.

Table 3.1 Selected properties of polyamide 6 and 6,6 [72]

Property	PA6	PA66
Density [g/cm^3]	1.06-1.16	1.1-1.18
Crystallinity [%]	30-40%	35-45%
Melting point [°C]	200-260	260-280
Modulus of Elasticity [GPa]	0.6-3	0.8-4
Tensile Strength [MPa]	60-80	70-90
Deformation [%]	40-120	30-100

One of the main problems related to polyamides is the worsening of mechanical properties due to water absorption. The water absorbed in the amorphous areas acts as a plasticizer weakening the hydrogen bonds. Very low percentages of absorbed water are enough to bring down the properties of polyamide. Table 3.2 shows how the tensile modulus of a PA6 changes with increasing water absorption. An absorption of 2.1% of water causes a 45% drop in the module, while at 3.9% the module falls to less than 30% of the initial value.

Table 3.2 variation of the PA6 tensile modulus in function of water absorbed [73]

Tensile modulus [MPa]	Absorbed water [%]
3040	0.4
1670	2.1
870	3.9
750	9.0

Water absorption is typically due to environmental humidity, which therefore plays a fundamental role in the treatment of polyamides. Table 3.3 shows how the flexural modulus changes between a dried polyamide sample and one exposed to 50% and 100% of relative humidity. Both for PA6 and PA66 an environment with 50% relative humidity causes a 60% drop in the value of the flexural modulus.

Table 3.3 variation of the flexural modulus for PA6 and PA66 as a function of relative humidity (R.H.) [73]

Polyamide	0% R.H.	50% R.H.	100% R.H.
PA66	3290 MPa	1295 MPa	600 MPa
PA6	2870 MPa	1225 MPa	500 MPa

Due to the humidity sensitivity of the polyamides it is necessary to carry out a drying operation before any technological process involving them. For example, considering polyamide pellets for injection moulding, if the drying operation is not carried out before moulding, the pellets would be processed with the absorbed water. In this way the material incorporates the water that evaporates at high temperature, forming bubbles that remain in the material in the form of porosity, worsening the properties of the material.

3.2 Glass fibers

Glass fibers are the type of fibers most commonly used, with carbon fibers, to reinforce composite materials, as they give stiffness and strength at a low cost [74].

Glass production represents for 55% of the entire ceramic industry, while within glass industry glass fibers account for 17% in the US market as shown in Figure 3.5.

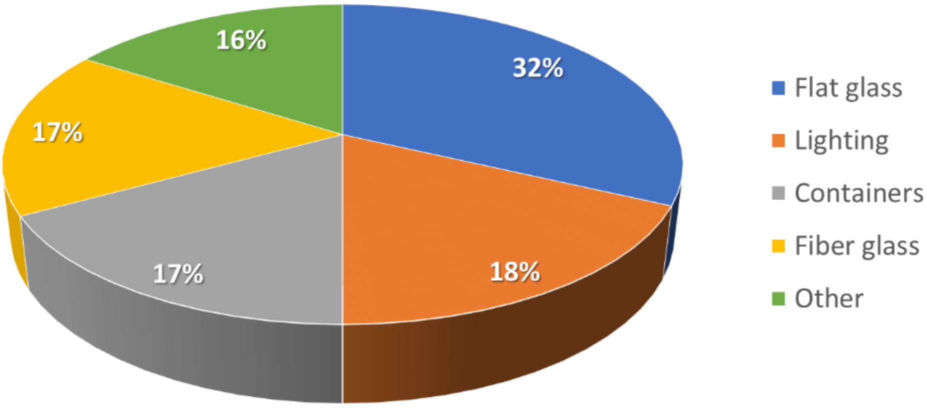


Figure 3.5 Overall glass market distribution in the United States [75]

The glass fibers are produced by using mainly the glass system SiO_2-Al_2O_3-CaO. The silica (SiO_2) is the oxide that generates the glass lattice, it is the major constituent of the amorphous phase and the one with higher viscosity in the molten state. Alumina (Al_2O_3) is an intermediate oxide that can partially replace silica, thus modifying the properties of the glass. These two oxides give an amorphous structure and grant good mechanical strength even at high temperature.

To increase the processability of the system, alkaline earth metal oxides are added. In fact, calcium oxide (CaO) interrupts the amorphous lattice, decreasing the viscosity of the glass and reducing the glass transition temperature. Other oxides that may be present in the glass system of fiberglass are B_2O_3, Na_2O, MgO, TiO_2 [76].

There are many types of glass fibers depending on the relative percentages of the oxides that make up the structure. The most used is E-glass whose typical chemical composition is shown below:

- SiO_2	52-56 %
- CaO	16-25%
- Al_2O_3	12-16 %
- B_2O_3	5-13 %
- Na_2O	0-2 %
- TiO_2	0-1,5 %

Table 3.4 summarizes the properties of E-glass fibers with a diameter of 12 μm. It can be seen how the density and the modulus are the same as flat glass depending on the chemical composition of the glass, while the strength assumes values in the order of gigapascals. The high strength of glass fibers is linked to their narrow section. In fact, in small volumes compared to the massive components, the probability of finding defects of critical dimensions that cause the fracture decreases [77].

Table 3.4 Selected properties of E-glass fiber [78]

Property	**Value**
Diameter	12 μm
Density	2,54 g/cm^3
Young Modulus	75 GPa
Strength	3,6 GPa
Elongation at break	2%

The production of glass fibers, sketch in Figure 3.6, is divided into the following steps [79]:

- **Batching**: depending on the type of glass, the oxides must be accurately weighed in exact quantities and mixed. The batching phase is now automated, so that under all the silos containing the oxides there is an automatic feeding and weighing system that takes the right amount of oxide and transfers it to the mixer.

- **Melting**: from the mixing station a pneumatic conveyor transfers the oxide mixture into a melting furnace typically divided into three parts. In the first part the temperature is 1500 °C and the components melt giving rise to a fluid and homogeneous molten glass. In the second part, at 1200 °C the molten glass is refined to eliminate gaseous product. The final part is kept at the processability temperature of the glass (950-1200 °C) and is the one in which the extrusion of the glass takes place. The approach just described involves direct melting of the glass in the fiber forming system. Another system that is currently not much used is the indirect melt or marble remelt. In this case the molten glass is cut into 15 mm marbles that are cooled and transported to the fiberization station.
- **Fiberization**: the glass fiber formation phase consists of a combination of extrusion and attenuation. The extrusion takes place through the passage of the molten glass in a die made up of many orifices (200-8000) produced in an erosion-resistant Pt/Rh alloy. The die is electronically heated, in order to grant the controlled temperature that maintains the viscosity of the glass constant. Out of the die a water jet cools the filaments which are mechanically drawing until they have a diameter in the 4-34 μm range.
- **Coating**: in the final phase of the fiberization the filaments are chemically coated with a size, consisting of lubricants, binders and coupling agents. Lubricants are used to protect the filament from abrasion and breakage, while coupling agents create chemical affinity between the surface of the fibers and the polymeric matrix.
- **Drying**: finally, the filaments are wrapped in strands made up of hundreds of filaments. Thus, glass fiber coils are obtained and dried in an oven. Now the product can be either sold directly or undergo additional processes to obtain chopped fiber, roving or yarn.

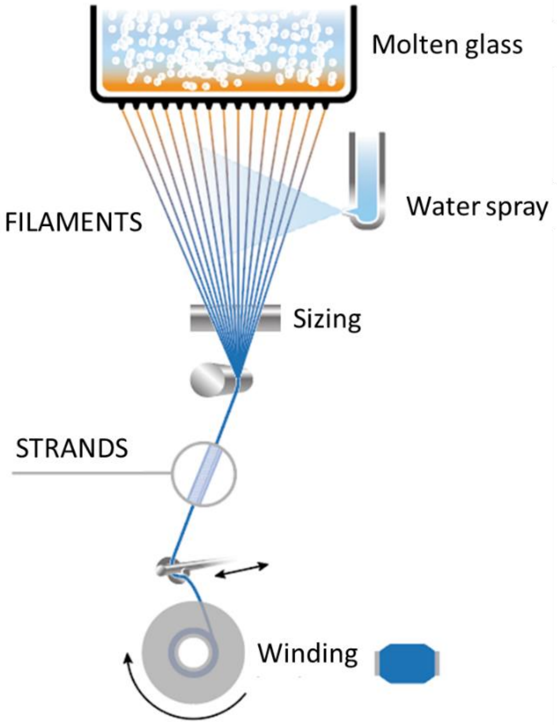


Figure 3.6 Schematic representation of a glass fiber production line [80]

The sizing operation is fundamental, since the problem that arises, from a technological point of view, is to disperse a polar reinforcement in an apolar matrix. In fact, the reinforcement effect of the glass fiber involves phenomena of transfer of the loads from the matrix to the fiber. Since this load transfer occurs at the interface between matrix and fiber, there must be a good interfacial interaction. For this reason, the interfacial properties of the fibers are modified by depositing an organic compound that creates a strong bond with the polymer matrix. The size deposited on the glass fibers can be different, depending on the kind of matrix. In the most common case, it is an alkoxysilane compound consisting of an organic group R’ and three alkoxy group OR. The alkoxysilanes are liquid compounds, whose alkoxy groups are easily hydrolysable to silanol groups (SiOH) according the reaction:

$$R' - Si(OR)_3 + 3H_2O \rightarrow R' - Si(OH)_3 + 3\,ROH \tag{3.1}$$

Therefore, by passing the glass fiber into an aqueous solution containing silanic size, the silanol groups will condense with the hydroxyl groups present on the surface of the glass fiber, leaving the fiber covered by the organic groups R' of the starting alkoxysilane. The silanization reaction is schematized in the Figure 3.7.

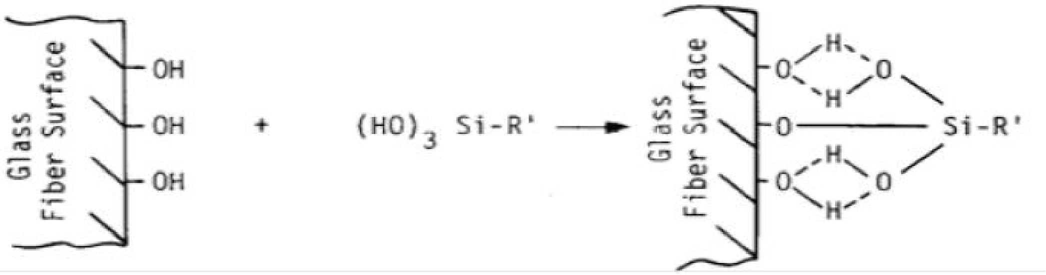


Figure 3.7 The silanization reaction at the glass fiber interface [81]

Depending on the polymeric matrix the most appropriate alkoxysilane is used, that is the one with the most compatible R' with the matrix. For example, if the glass fibers are to be dispersed in an epoxy matrix, an alkoxysilane with an epoxy ring or an amino group is used. In this way the amino group can participate in the cross-linking and become chemically bond with the matrix.

3.3 Mechanical properties of composite materials reinforced with short fibers

The mechanical properties of a composite material depend on both the matrix and the reinforcement properties and on the quality of the interface between the two phases.

The evaluation of the mechanical properties of a composite material takes place through the formulation of models. The simplest model consists of a composite in which the following hypotheses are valid [78]:

1. all the fibers are perfectly aligned with each other and in the longitudinal direction
2. the interfacial bond between fiber and matrix is perfect, fibers and matrix cannot slide mutually
3. fiber and matrix have the same Poisson’s ratio

Under these assumptions, if the load is applied in the longitudinal direction, the mechanical properties of the composite can be easily predictable using the rule of mixtures:

$$E_c = E_f V_f + E_m (1 - V_f) \tag{3.2}$$

$$\sigma_c = \sigma_f V_f + \sigma_m (1 - V_f) \tag{3.3}$$

Where:

E_x Young modulus of composite (c), fiber (f) and matrix (m)

σ_x tensile strength of composite (c), fiber (f) and matrix (m)

V_f Volume fraction of fibers in the composite

The simple model based on the mixture rule must be modified considering the type of composite in detail. In the case of a thermoplastic matrix reinforced with glass fibers, the matrix is ductile and the fibers are brittle and stiff. If the fiber content is greater than a critical value, it can be assumed that the load is supported above all by the fibers. By subjecting the composite to traction, the fibers deform linearly and elastically until they reach the ultimate breaking strength σ_{fu}. At this point the entire composite breaks while the matrix is subjected to a load value σ'_m lower than the maximum one σ_m. Based on these considerations equation (3.3) must be modified as follows:

$$\sigma_c = \sigma_{fu} V_f + \sigma'_m (1 - V_f) \tag{3.4}$$

The model based on long unidirectional fibers must be modified in the case of composites with short fibers for both elastic and plastic behaviour. In the case of composites with long continuous fibers the break occurs in conjunction with the fracture of the fibers. Instead, in the presence of short fibers the phenomena of debonding become fundamental. The matrix can lose adhesion with the fibers, making ineffective the load transfer. There is no debonding until the shear stress present at the fiber-matrix interface is sufficient to balance the tensile stress. This shear stress is proportional to the surface of the fiber and, therefore, only sufficiently long fibers are able to effectively transfer the loads avoiding the debonding.

Therefore, the minimum length of the fibers necessary to completely transfer the load is defined as critical length. The diameter of the fiber that contributes to determining the size of the interface between fiber and matrix must also be taken into consideration. Therefore, a geometric critical aspect ratio, proposed by Cox [82], is defined as follows:

$$\frac{l_c}{d} = \frac{\sigma_f}{2\tau_i} \tag{3.5}$$

Where:

l_c critical length of the fiber

d diameter of the fiber

τ_i interface shear stress

σ_f tensile strength of the fiber

Another aspect to be considered is that the reinforcement effect of the fibers also depends on their orientation. The more the fibers are oriented in the direction in which the load is applied, the more they will contribute to reinforce the material.

Hence, the model previously exposed based on the rule of mixtures must be modified in the case of short fibers, taking into consideration two effects that reduce the effectiveness of the fibers in reinforcing the composite:

- Efficiency parameter η_l: which considers the fiber aspect ratio
- Krenchel parameter η_θ: which takes into account the orientation of the fiber

The evaluation of the elastic modulus of the composite thus becomes:

$$E_c = \eta_l \eta_\theta E_f V_f + E_m(1 - V_f) \tag{3.6}$$

The evaluation of the strength of the composite containing short fibers will depend on the length of the fibers. If the fibers are longer than the critical length they will be able to effectively transfer the load to a length equal to 1-l_c. In fact, the fiber ends do not transfer the load entirely as the fiber/matrix interface is interrupted.

In this case the stress that the fiber supports will be an average value between central and terminal parts which takes on value:

$$\bar{\sigma_f} = \sigma_{fu}\left(1 - \frac{l_c}{2l}\right) \tag{3.7}$$

Where:

$\bar{\sigma_f}$ average stress in the fiber

σ_{fu} ultimate breaking strength of the fibers

l_c critical length of the fiber

l length of the fiber

The rule of mixture becomes:

$$\sigma_c = \sigma_{fu}\left(1 - \frac{l_c}{2l}\right)V_f + \sigma'_m(1 - V_f) \tag{3.8}$$

On the other hand, if the fibers are shorter than the critical length, the stress sustained by the fiber/matrix interface and then the strength of the composite depends on the shear stress on the interface, according the equation:

$$\sigma_f = \frac{l \cdot \tau_i}{d} \tag{3.9}$$

The mixture rule must be modified considering that for fibers shorter than the critical length the ultimate strength of the matrix σ_{mu} must be considered:

$$\sigma_c = \frac{l \cdot \tau_i}{d}V_f + \sigma_{mu}(1 - V_f) \tag{3.10}$$

Also in this case the effect of fiber orientation can be taken into consideration by using the Krenchel parameter. In this case equations (3.8) and (3.10) become:

$$\sigma_c = \eta_\theta \bar{\sigma_f} V_f + \sigma'_m(1 - V_f) \tag{3.11}$$

$$\sigma_c = \eta_\theta \frac{l \cdot \tau_i}{d}V_f + \sigma_{mu}(1 - V_f) \tag{3.12}$$

Chapter 4

Materials and methods

The investigation on the recyclability of a composite material made of polyamide matrix reinforced with short glass fibers was carried out on two different types of product: an end-of-life component and a processing scrap.

In this chapter the first two sections show the mechanical recycling procedures of the two different composites. Then the technologies and the analysis techniques used for the characterization are reported.

4.1 Mechanical recycling of end-of-life component

The end-of-life component under investigation was the radiator cooling system (Figure 4.1) of a FCA vehicle recovered from a car disposal plant, made up of polyamide 6,6 reinforced with 35% glass fibers.

Figure 4.1 Radiator cooling system made of polyamide 66 reinforced with 35% of glass fibers

The component during its life cycle, which is assumed to be over 10 years, is subjected to degradation due to multiple factors. First of all, being a component located close to the engine, it is subject to continuous thermal cycling which can cause dimensional distortions and degradation of the polymer matrix. In addition, the component is subject to environmental factors such as weather and seasonal temperature changes and not high impacts due to gravel on the road.

The components at the end of their life have been washed to remove the pollutants accumulated during the life cycle, they were then cut with a Globe KB-45 band saw and subsequently pelletized with a PIOVAN granulator.

The pellets obtained from the granulator were dried at a temperature of 80°C for 16h and then injection moulded to obtain tensile and bending specimens, called R as recycled.

The grinding and injection moulding phases were repeated two more times, obtaining two other products, called RM1 and RM2 as they were re-moulded one or two times. The mechanical recycling procedure adopted is described in the Figure 4.2.

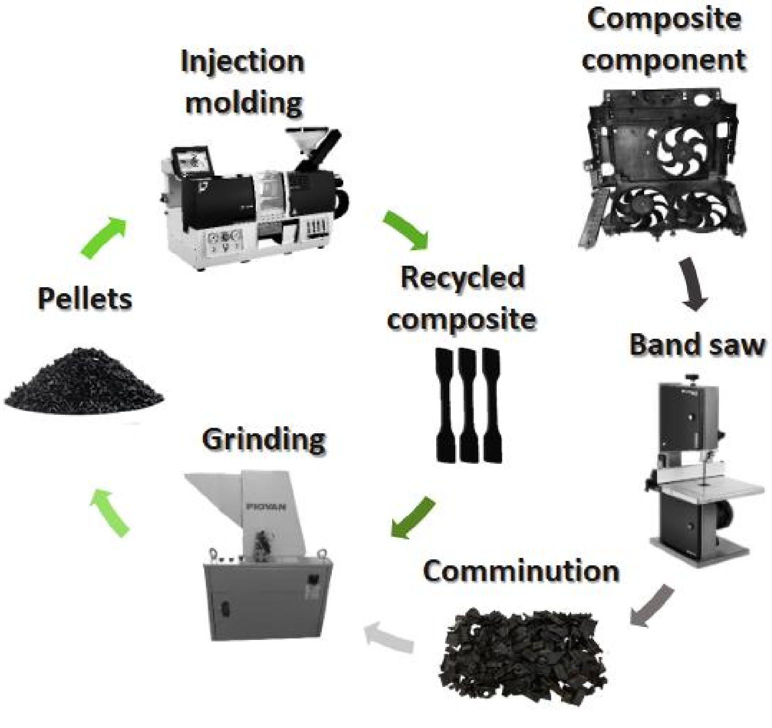


Figure 4.2 Schematic illustration of the mechanical recycling method

The products obtained after the mechanical recycling were then compared with a reference material made of 35% glass fiber reinforced polyamide, to date currently used to produce the same type of components. It should be stressed that it was not possible to find exactly the same material used for the manufacture of the component, as this was recovered in the context of waste management and produced at least ten years before this study.

To sum up, 5 type of products have been obtained and characterized:

- **End of life (EoL)**: end-of-life product deriving from the pelletizing of the radiator cooling system. It is a composite made of polyamide 6,6 reinforced with 35% glass fiber. On this product it was evaluated the effect of degradation occurred on the component during its life cycle that can be estimated at more than 10 years.
- **Recycled (R)**: it is the product deriving from the recycling of the component at the end of its life. This material, in addition to natural aging has undergone reworking by injection moulding.
- **Remoulded one times (RM1)**: product resulting from the grinding and remoulding of R. As there was no natural aging of the product R, RM1 can be classified as recycling of processing scraps of R.
- **Remoulded two times (RM2)**: product resulting from the grinding and remoulding of RM1. As there was no natural aging of the product RM1, RM2 can be classified as recycling of processing scraps of RM1.
- **Reference material (Ref)**: the reference material consists of RADILON A RV350W pellets, purchased by Radici Group. This is a polyamide 6,6 reinforced with 35% of glass fibers, and nowadays used by FCA to produce the same type of component.

4.1 Mechanical recycling of processing scraps

The purpose of the second experimental activity is to present how composite processing scraps, deriving from thermoforming process, can be recycled mechanically.

In this case the product to be recycled was a laminate produced by BOND Laminate Lanxess with the trade name TEPEX dynalite 103-RG600(x)/47% Roving Glass (Figure 4.3). It is a laminate with 47% by volume of reinforcement consisting of a polyamide 6 matrix reinforced with a twill-weave textile of continuous glass fibers. The term twill-weave fabric means that one warp fiber alternately weave over and under two weft fibers in a regular repeated manner.

The scraps under examination derive from the parts of the laminate present around the mould and therefore does not undergo the thermoforming process, but only a thermal cycling. For this reason, the thermal history of the laminate was first simulated by placing the scraps in an oven at 200 °C for 8 hours.

The laminate was then reduced in size by a Globe KB-45 band saw and subsequently pelletized with a PIOVAN granulator.

Figure 4.3 Laminate made of polyamide 6 reinforced with 47% roving glass fibers before and after grinding.

Unlike the mechanical recycling procedure of the end-of-life component described in the previous paragraph, in this case it was necessary to carry out a compounding operation before forming.

In fact, the laminate has a fiber content of 47% by volume, which, being the matrix and composite densities respectively equal to 1.14 g/cm^3 and 1.8 g/cm^3, is equivalent to 66.4% by weight. A material showing a percentage of fibers of more than 60% is very difficult to reprocess, consequently the ground laminate was mixed with virgin polyamide 6 to obtain a 30 wt.% glass fiber composite.

The virgin polyamide 6 is marketed by the same manufacturer of the laminate with the name of Durethan B30S and is designed for injection moulding.

It was not possible to injection-mould the composite with 30% glass fiber, since the material does not have the rheological characteristics suitable for this forming process. It is important to point out that the injection moulding was carried out with a BABYPLAST 6/10P laboratory machine that, as explained in the paragraph on injection moulding, does not possess all the characteristics of an industrial machine. Therefore, it cannot be excluded that an industrial injection moulding press can process the recycled 30% glass fiber composite product.

The 30% glass fiber composite was therefore compression moulded, using a COLLINS press, to obtain 150x10x3 mm dog bone flat specimens. The moulding was carried out with a preheating at 260°C for 3 minutes, followed by degassing and finally by applying a pressure of 100 bar at 260°C for another 3 minutes.

In order to obtain an injection mouldable product, a further mixing with virgin PA6 was carried out to obtain a composite at 15% by weight of glass fibers. The composite material thus obtained was pelletized and moulded both by injection and by compression moulding.

Furthermore, in order to investigate the differences that the two technologies determine in terms of final mechanical properties, without considering the charge effect, compression and injection moulded virgin PA6 samples have been realized.

To sum up, 5 different types of products have been obtained:

- Compression moulded polyamide 6, used as a reference (CM PA6)
- Compression moulded polyamide 6 reinforced with 15 wt.% of short glass fibers (CM PA6+15%GF)
- Compression moulded polyamide 6 reinforced with 30 wt.% of short glass fibers (CM PA6+30%GF)
- Injection moulded polyamide 6, used as a reference (IM PA6)
- Injection moulded polyamide 6 reinforced with 15 wt.% of short glass fibers (IM PA6+15%GF)

4.3 Injection moulding

Injection moulding is one of the most common manufacturing technologies for thermoplastic polymers. It is characterized by high productivity and low costs as well as by a wide process versatility. In fact, with this technology it is possible to obtain objects of complex shape and with dimensions ranging between few millimetres and few meters.

The process uses material in the form of pellets as input, which is gradually plasticized and then injected into a mould to acquire the final shape.

The injection moulding machine con be divided into two parts (Figure 4.4):

- Plasticating unit:
- Injection and clamping unit:

The plasticating unit is responsible for the melting of the material, while the injection and clamping unit allows the material to be introduced into the mould and to preserve the ideal conditions for a correct filling.

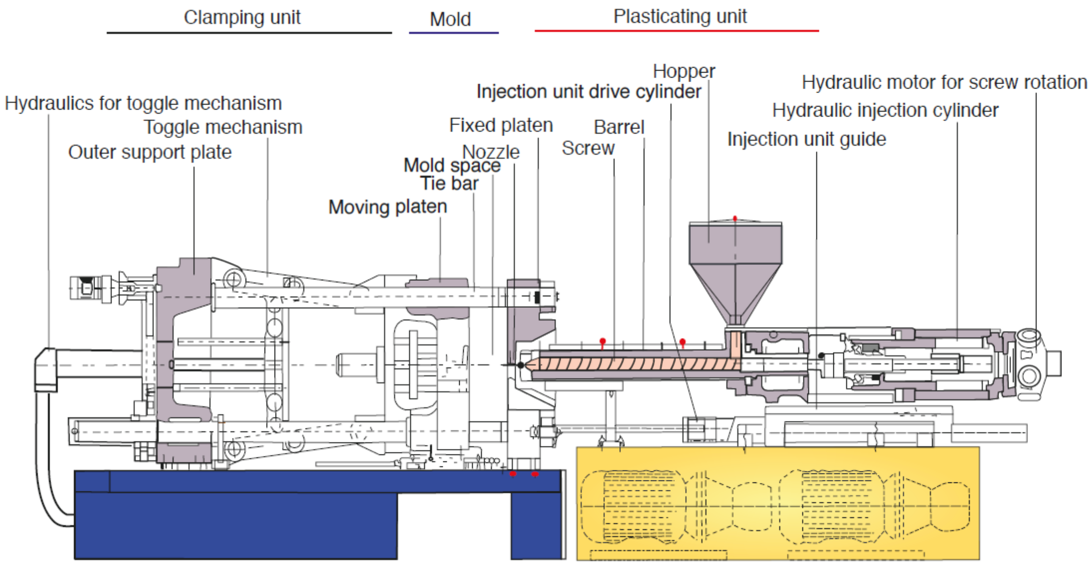


Figure 4.4 Schematic of an injection moulding machine [72]

The process begins with the insertion of the pellets in the hopper, which continuously feeds the plasticating group. It consists of a heated barrel equipped with the plasticizing screw. The screw has length L and variable diameter along the length of the screw. The plasticization of the polymer is due both to the heat supplied by the resistances placed on the cylinder and to the heat due to the mechanical friction between the material and the screw. Plasticization allows the achievement of the viscosity conditions suitable for filling the mould.

The material is introduced into the mould through the injection and clamping unit. The material is pushed to pass the nozzle through the advancement of the punching screw and the pressure applied by the material, continuously introduced into the feeding zone. Once the cavity is filled, a holding pressure is maintained to compensate for material shrinkage.

The mould is equipped with cooling channels to allow conditioning and avoid temperature gradients inside that part. Once cooled, the product is extracted from the cavity by using the extraction system.

Injection moulding machine are classified according to the $\boldsymbol{T/P}$ ratio, where T is the clamping force in tons and P id defined as follows:

$$P = \frac{V_{max} p_{max}}{100} \tag{4.1}$$

Where:

V_{max} maximum shot size in cm^3

p_{max} maximum injection pressure in bar

For this study a BABYPLAST 6/10P injection moulding machine was used. This is a laboratory machine that allows small quantities of material (in the order of hundreds of grams) to be processed, while industrial presses require the feeding of many kilograms. It is a compact machine, as shown in Figure 4.5, which is not equipped with a plasticizing screw. In this case plasticization is guaranteed by the movement of heated steel spheres. Therefore, the material is subject to little friction and remains in temperature for a short time due to the small dimensions of the injection unit. In this case, the plasticating unit consists of three heated zones at different temperatures H1, H2, H3; where H1 is the temperature of the zone near the hopper and H3 is the temperature of the zone near the injection unit.

Figure 4.5 Babyplast injection moulding machine

This machine was used for the production of tensile and flexural specimens necessary for the mechanical tests on the composites. The difference between the two types of specimens consists in the mould used: dog bone specimens for the tensile test and parallelepiped bars for the bending test. The different geometry of the mould cavity implies different amounts of injected material, different surface/volume ratio and consequently different cooling speed.

Table 4.1 shows the moulding conditions used for the products deriving from the mechanical recycling of the end-of-life component made of glass fiber reinforced polyamide 6,6. The velocity of first injection is used for filling the mould, while the second injection pressure is adopted for the holding phase. For all specimens the mould was conditioned at 90°C.

Table 4.1 Injection moulding conditions used to produce tensile (Tens) and flexural (Flex) specimens made of 35% glass fiber reinforced polyamide 6,6 for reference (ref), recycling (R) and remoulded (RM1, RM2) composites

Material	Ref		R		RM1		RM2	
Specimen	Tens	Flex	Tens	Flex	Tens	Flex	Tens	Flex
H1 [°C]	290	300	283	280	280	280	285	285
H2 [°C]	295	305	288	285	285	285	290	290
H3 [°C]	295	305	283	280	280	280	285	285
Shot size [mm]	20	28	14	15	13	15	13	15
Cooling time [s]	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5
I injection pressure [bar]	120	130	100	100	100	100	100	100
I injection time [s]	10	5	7	7	7	7	7	7
I injection velocity [%]	40	40	40	40	40	40	40	40
II injection pressure [bar]	100	110	80	80	80	80	80	80
II injection time [s]	25	8	25	25	25	25	25	25
II injection velocity [%]	30	30	30	30	30	30	30	30

4.4 Thermal analysis

In this study thermogravimetric analysis (TGA) and differential scanning colorimetry (DSC) have been performed for thermal investigations.

Thermogravimetric analysis evaluates the weight loss of the polymeric material as the temperature increases. As output a graph is obtained with the temperature on the abscissa axis and the residual weight percentage of the material on the ordinate axis.

In the case of polymeric materials, by setting the temperature ramp, the thermal stability of the sample is evaluated, obtaining the following indications:

- **The initial degradation temperature**: the temperature is conventionally associated with a 2% weight loss.
- **Degradation mechanism**: can be evaluated based on the number of steps present in the curve, since the number of steps required for degradation allows to hypothesize the mechanism.
- **Percentage of residue**: the presence of a residue stable at high temperatures may be due to the formation of char or the presence of inorganic fillers, as is the case of glass fiber reinforced composite materials.

The test can be performed in an inert atmosphere (Ar) to evaluate the thermal degradation or in an oxidizing atmosphere, usually air, to evaluate the thermoxidative degradation.

TGA tests in Argon or Air atmosphere were performed with a METTLER TOLEDO TGA/SDTA851e instruments with this condition:

- Temperature range	T = 25 – 800 °C
- Heating rate	dT/dt = 10 °C/min
- Gas flow	50 ml/min

Differential scanning calorimetry (DSC) is a thermal analysis technique used to study the behaviour of a material following a controlled heating (or cooling). The word *differential* in the name implies that the instrument that performs the analysis does not calculate the amount of energy needed to obtain a given temperature increase in the sample, but rather the difference in energy needed to keep sample and reference at the same temperature, by compensating through additional heat system the exothermal or endothermic effect occurring in the sample.

DSC is very useful in the study of phase transitions. In fact, before a phase transition, the energy difference between the sample and the reference is constant. When the sample undergoes a transition, the sample heater must provide additional energy to the sample for endothermic transition or less energy for exothermic transition to maintain equal the sample and reference temperature. The result of the analysis is expressed in the form of a two-dimensional graph that shows the temperature on the abscissa and the difference between the heat flows supplied to the sample and the reference on the ordinates.

In the case of polymeric materials, the DSC technique allows to calculate:

- Melting temperature
- Crystallization temperature
- Crystallinity percentage
- Glass transition temperature

DSC tests were performed with a PERKIN ELMER PYRIS 1 instruments under argon atmosphere with these conditions:

- Temperature range for heating ramp	25-300 °C
- Temperature range for cooling ramp	300-25°C
- Heating rate	10 °C/min

For each sample, two identical cycles were performed under the conditions listed above. The first cycle eliminates the thermal history of the sample, while the second cycle concerns only the material.

4.5 Mechanical tests

The mechanical characterization of the recycled composites was carried out by tensile and flexural tests. The tensile test was carried out for both recycling studies, while the bending test was performed only for the samples recycled from the end-of-life component.

Since all the samples are of polyamide matrix, before the tests they were dried at 80°C for 16 hours. For both types of mechanical test it was used a MTS Criterion Model 43 machine with a 5 kN load cell.

Tensile tests were carried out according to ISO 527, using a 25 mm contact resistive strain gauge, a preload of 5 N and a crosshead speed of 1 mm/min. Injection moulded specimens were 5A dog bone type of 75x4x2 mm size, while compression moulded specimens were 1B dog bone type of 150x10x4 mm size [83].

From the tensile tests the values of tensile strength, elastic modulus and elongation at break were obtained. As regards the evaluation of the module, this took place taking into consideration the slope of the linear elastic part between 0.05% and 0.25% of deformation, as required by the standard [84].

The three-point bending test was performed according to ISO 178, using a 2 N preload, a crosshead speed of 2 mm/min and a distance between supports (span) of 48 mm. In this case the specimens had a flat rectangular shape with dimensions 75x6x3 mm. Bending strength and modulus were evaluated according the following equations [85]:

$$\sigma_f = \frac{3\,F\,l}{2\,b\,h^2} \tag{4.2}$$

$$E_f = \frac{F\,l^3}{4\,b\,h^3\delta} \tag{4.3}$$

where:

σ_f	is the flexural stress in megapascals
E_f	is the flexural modulus of elasticity in megapascal
F	is the load in newtons
l	is the span in millimetres
b	is the width of the specimen in millimetres
h	is the thickness of the specimen in millimetres
δ	is the deflection of the specimen in millimetres

4.6 Optical microscope analysis

The optical microscope investigation allowed to evaluate different aspects of the nature of the composite material:

- Sample morphology
- Fiber orientation
- Fiber length

The samples were prepared by sectioning the tensile specimens with a BUEHLER ISOMET 4000 linear precision saw equipped with a diamond blade with feed speed of 2 mm/min and rotation speed of 1800 rpm. Subsequently the samples were mounted with a two-component methacrylic based resin (KULZER TECHNOVIT 4006). The mounting samples were polished with a PRESI MECATECH 234 machine using SiC abrasive papers. The optical microscope images were acquired with the LEICA DMI50000 instrument with magnifications in the range of 50x-1000x.

The fiber length was evaluated with the optical microscope after burning the matrix in a furnace. Once the fibers were recovered, they were placed on a glass slide and observed under the microscope in order to measure their length. From the measurement of more than 200 fibers it was possible to obtain the fiber length distribution.

For the evaluation of the fiber orientation was developed a Matlab program, that, starting from a series of images taken with an optical microscope, is able to extrapolate the orientation of the fibers with respect to the axis of the specimen. The program is based on the principle that a fiber perfectly perpendicular to the surface will be seen as a perfect circle under the microscope. In this case the software assigns a θ angle of zero degrees, where θ is the angle that is formed between the fiber and the axis of the specimen. Instead, fibers misaligned with respect to the axis of the specimen will be seen as ellipses.

As shown in Figure 4.6, the major axis of the ellipse a is geometrically related to the fiber diameter d through the trigonometric equation:

$$d = a \cdot \cos\theta \tag{4.4}$$

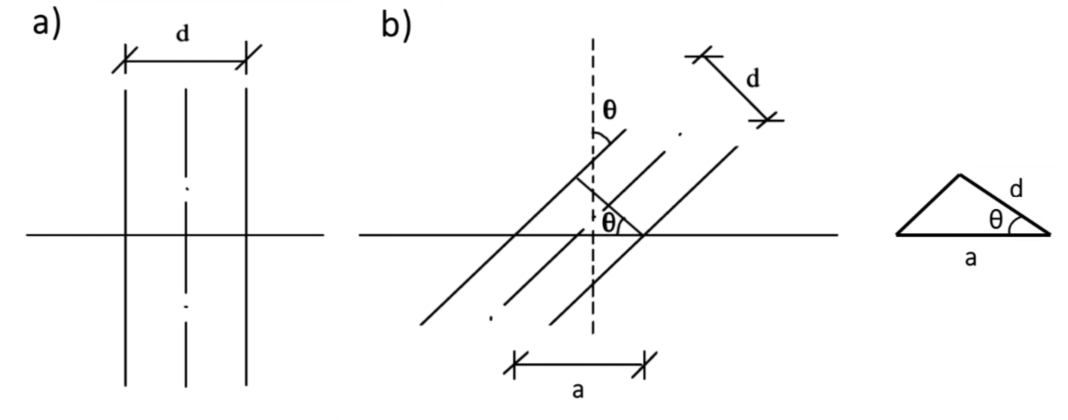


Figure 4.6 Schematic representation of (a) a fiber parallel to the axis of the specimen and (b) a fiber misaligned of a θ angle with respect to the axis of the specimen.

Therefore, as the theta angle increases, the fiber will be increasingly misaligned resulting in the image as an ellipse more and more elongated.

It is important to note that for small theta values it is very difficult to visually evaluate the difference between a circular and an elliptical geometry. Assuming a fiber diameter of 10 µm, the table 4.2 shows the values that the major axis *a* of the ellipse assumes as the *θ* angle varies. For example, an inclination of 10° provides an increase in the major axis of the ellipse by only 1%, at 20° by 6% and at 30 by 15%. On the contrary, by closer to 90°, small variations of *θ* cause large variations in the size of the axis *a*.

Table 4.2 length of the major axis *a* of the ellipse when varying the misaligned angle θ, according to equation 4.4, assuming a diameter of 10 µm.

Misaligned angle *θ*	**Ellipse major axis *a***
0°	10 µm
5°	10.04 µm
10°	10.15 µm
20°	10.64 µm
30°	11.55 µm
40°	13.05 µm
60°	20 µm
70°	29.24 µm
80°	57.59 µm

The Matlab program as input requires the fiber diameter and an image taken with the optical microscope. The higher the contrast between the matrix and the fibers, the more the program can adequately distinguish the fibers and assign the right angle. In fact, there is a threshold value on grayscale below which the software identifies the fiber in the image. To distinguish the fibers from any other particles present, the software evaluates if the minor axis of the ellipse is compatible with the indicated diameter.

At the end of the process the software generates a histogram with the orientation distribution of the fibers according to the θ angle (Figure 4.8), returns the input image showing the detected fibers with crosses (Figure 4.7), and indicates the average θ angle value for that image or set of images. From the image it can be seen how the main errors the program may incur are either not to consider fibers or to misinterpret contact fibers seeing them as a single fiber.

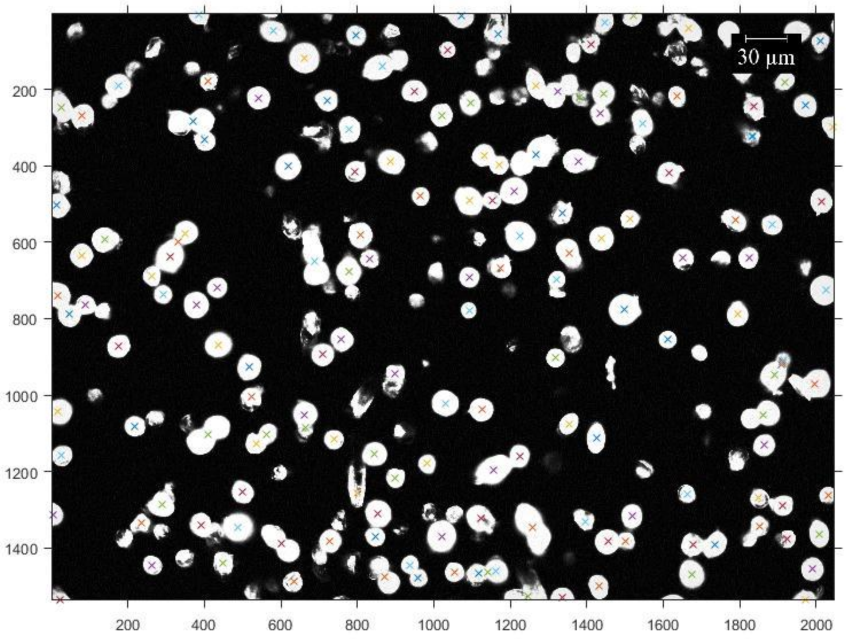


Figure 4.7 Optical microscope image (200x) with the fibers identified by the MATLAB program

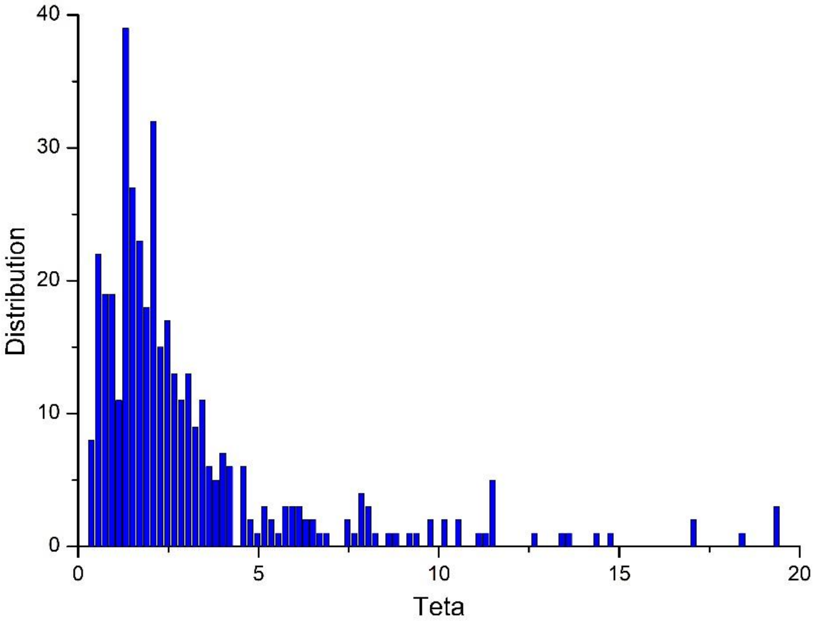


Figure 4.8 Histogram of the orientation of the fibers in the angle range 0-20° supplied as output by the Matlab program

4.7 Rheological measurements

The degradation of the polymeric matrix following the recycling operations can be investigated by evaluating the change in viscosity.

Viscosity is a characteristic of materials that describes the resistance to deformation of a fluid. In particular, the viscosity can be expressed as correlation between shear rate and shear stress. If the viscosity does not change as the shear rate changes, the fluid is defined as Newtonian and follows Newton's law:

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{4.5}$$

Where:

η viscosity $[Pa \cdot s]$

τ shear stress $[MPa]$

$\dot{\gamma}$ shear rate $[s^{-1}]$

The polymers do not have a Newtonian behaviour, since their viscosity decreases as the shear rate increases. This type of fluids called pseudoplastics are described with a power law with (n<1):

$$\eta = k \cdot \dot{\gamma}^{n-1} \tag{4.6}$$

In the case of polymeric materials at low shear rate also the polymers behave like Newtonian fluids maintaining constant the viscosity. This happens because the time of application of the deformation is much greater than the relaxation time of the polymeric structure. On the other hand, as the shear rate increases, the polymeric structure does not have the time to rearrange randomly, and then the macromolecules remain oriented with a consequent decrease in viscosity.

The effect of reduction in viscosity at high rates of deformation is defined *shear thinning*. Figure 4.9 shows the shear thinning effect for different thermoplastic polymeric materials.

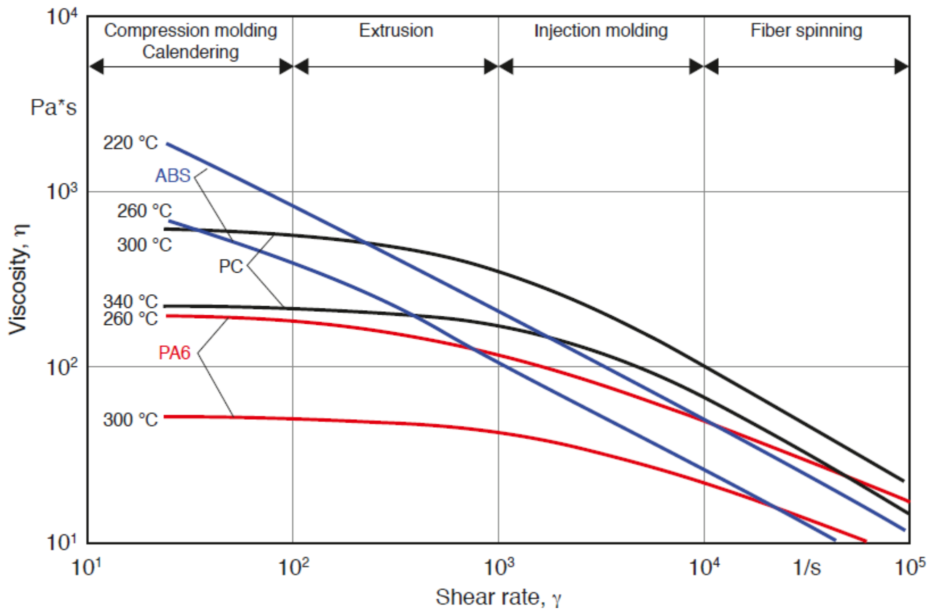


Figure 4.9 Viscosity curves for a selected number of thermoplastic polymers [72]

In this study the viscosity evaluation took place using a strain-controlled Rheometer Ares with parallel plates of 25 mm. The measurements were performed in a nitrogen atmosphere at temperature of 290 °C and a deformation of 0.25%. The same temperature used for injection moulding was chosen, in this way the rheological properties of the polymer were analysed in the same temperature conditions of the transformation process.

4.8 Density measurements

The density measurements were made according to the ISO 1183 standard entitled “Methods for determining the density of non-cellular plastics” [86]. In particular, it was applied the immersion method, which involves the use of an apparatus shown in Figure 4.10:

1. Analytical balance
2. Immersion vessel
3. Stationary support

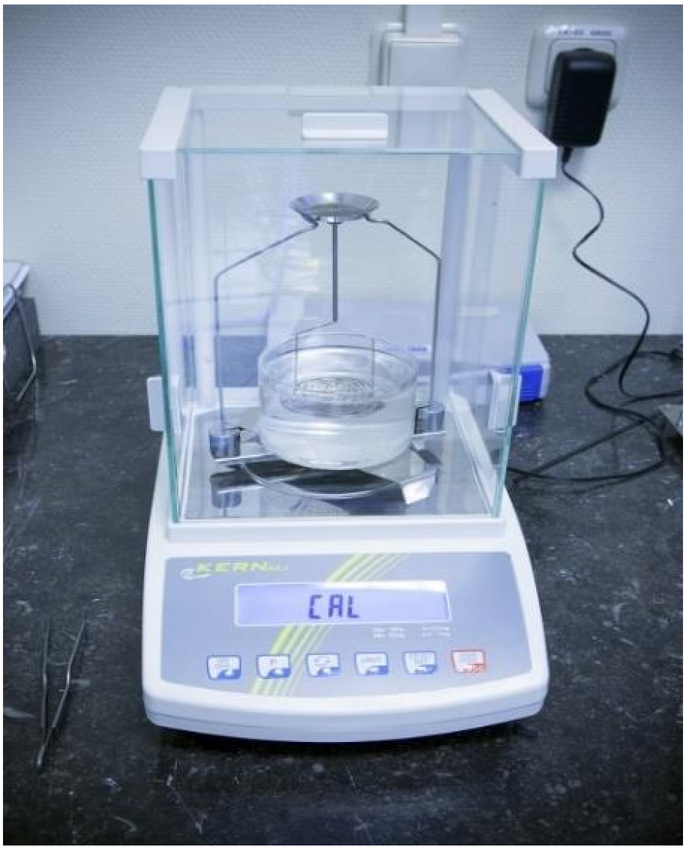


Figure 4.10 Apparatus for density measurements with immersion method

The density is calculated by performing two weighing, one in air and a second in the immersion liquid. In this case distilled water was used as the immersion liquid.

Knowing the density of the immersion liquid and the masses measured by the two weighing, the density is calculated according to the following equation:

$$\rho_S = \frac{m_{S,A} \cdot \rho_{IL}}{m_{S,A} - m_{S,IL}}$$

where:

ρ_S is the density of the specimen, in grams per cubic centimetre

ρ_{IL} is the density of the immersion liquid, in grams per cubic centimetre

$m_{S,A}$ is the apparent mass, in grams, of the specimen in air

$m_{S,IL}$ is the apparent mass, in grams, of the specimen in the immersion liquid

Chapter 5

Mechanical recycling of an end-of-life automotive composite component

In this research activity the possibility of mechanically recycle an end of life automotive composite component was investigated. The component consists of a polyamide 6,6 matrix reinforced with 35% short glass fibers.

For clarity, Table 5.1 shows the abbreviations used to indicate the different types of composite material.

Table 5.1 Abbreviations used to indicate composite materials at the different recycling steps

Abbreviation	Material
EoL	End of life
R	Recycled
RM1	Remoulded one time
RM2	Remoulded two times
Ref	Reference

5.1 Thermal and XRD analysis

First, the thermoxidative behaviour of the composite was investigated by performing thermogravimetric analysis (TGA) in air. From the TGA measurements it was possible to derive the initial degradation temperature, conventionally set to the temperature at which a weight loss of 2% of the material occurs, and the solid residue at 800 °C. In the case of composite materials, the solid residue can be associated to the reinforcing phase or to the presence of non-volatilized additives. For this reason, TGA analysis was carried out in an oxidizing atmosphere, because the presence of oxygen facilitates the combustion of organic additives (like carbon black), and then allows a more accurate estimation of the weight percentage of the reinforcing phase.

From the TGA curves in Figure 5.1 it can be seen that the degradation occurs in a single step with a continuous decrease in weight, according to the thermoxidative degradation mechanism of polyamide 6,6 which leads to the cleavage of the chain due to the formation of radicals [87,88]. The reference material differs slightly by presenting a step in the terminal part, probably due to the presence of different additives with respect to the material of the component at the end of its life.

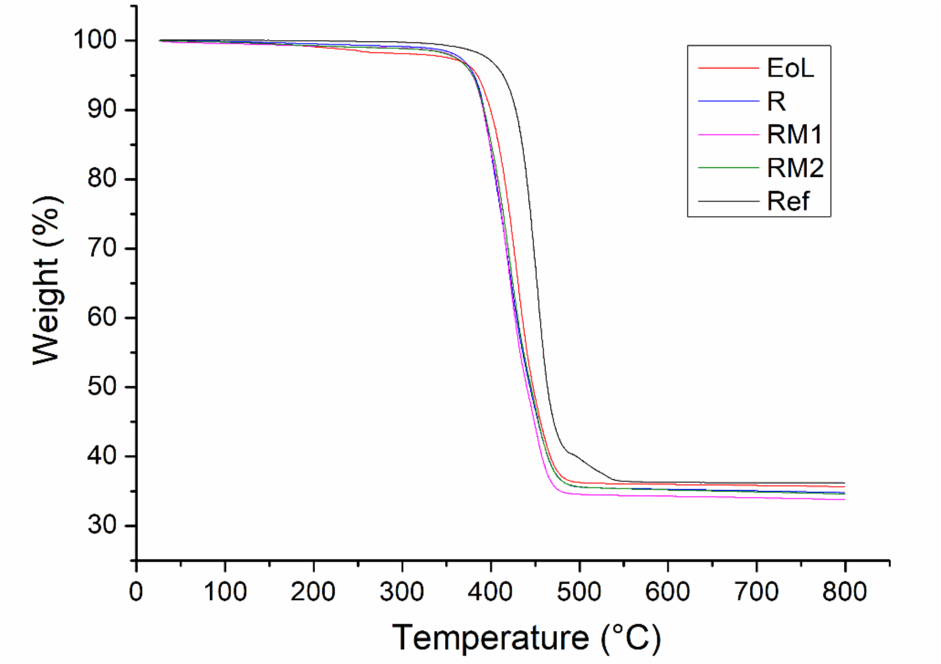


Figure 5.1 TGA analysis performed in air of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

The initial degradation temperature (Table 5.2) is always above 300 °C, passing from the 322 °C for the end of life component to just over 350 °C for the reprocessed products, and up to the 389 °C for the reference material. As regards the solid residue, the results obtained demonstrate the comparability between the end-of-life component and the reference material. In fact, all composite products have a fiber percentage around 35%.

Table 5.2 Initial degradation temperature and residue of PA66GF composites

Sample	$T_{2\%}$ [°C]	Residue [%]
EoL	322,1	35,7
R	358,8	34,8
RM1	353,2	33,8
RM2	351,3	34,6
Ref	389,2	36,2

The thermal characterization of the material was also carried out by differential scanning calorimetry. The investigation was conducted by performing two heating/cooling cycles of the different products. The first cycle (Figure 5.2) takes into account the forming process of the component, while the second one (Figure 5.3), due to the slow cooling during the first cycle, returns the characteristics of the material irrespectively from its thermal history.

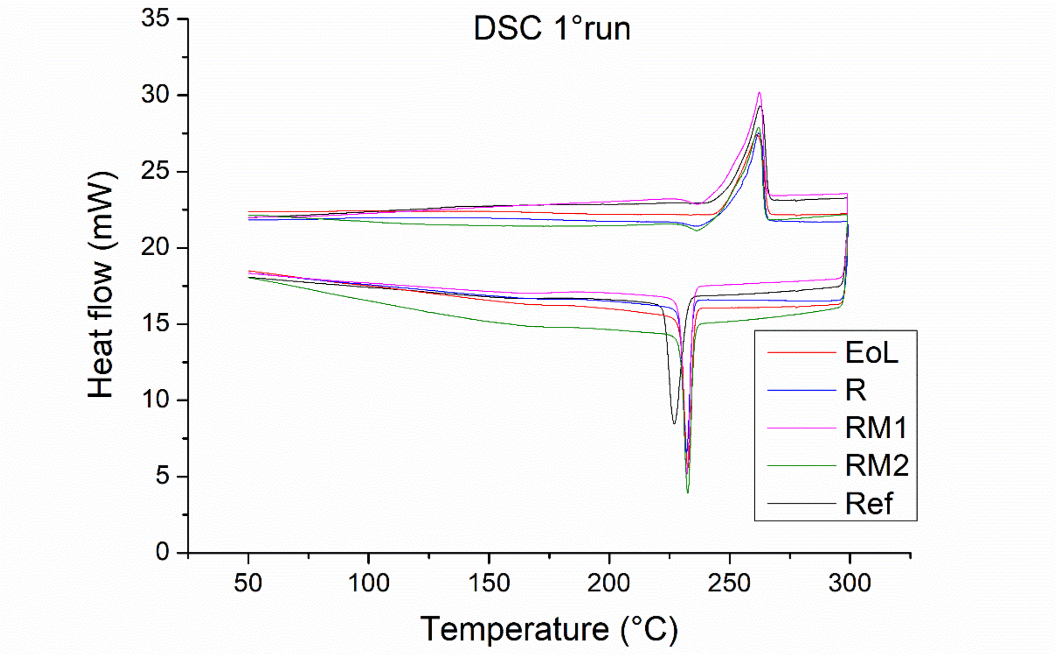


Figure 5.2 DSC curves related to first heating/cooling run of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

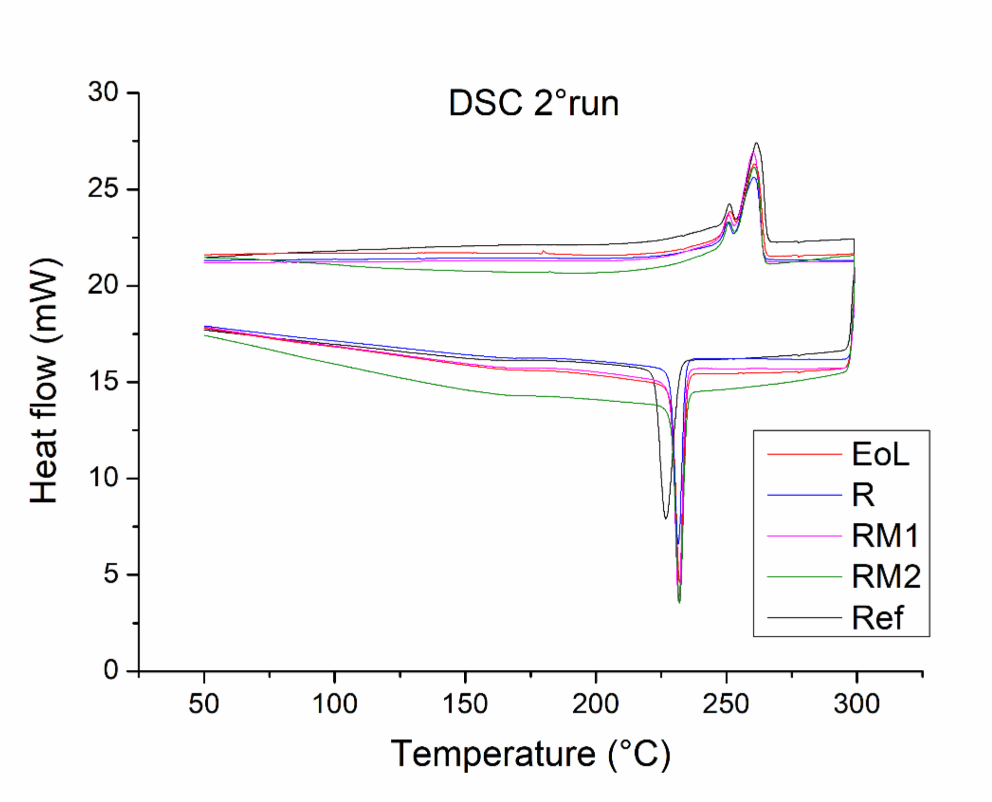


Figure 5.3 DSC curves related to second heating/cooling run of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

The main difference in the comparison between the two cycles is the melting peak. The first cycle shows that all samples present a single endothermic peak, while DSC curves related to second heating/cooling run show double endothermic peak in the same temperature range of the first run. The difference between the first and second run, and in particular the presence of a double peak, may be due both to polyamides polymorphism and to cooling speed rate. In fact, during the crystallization small, imperfect and disoriented crystallites [89,90], that melt at a slightly lower temperature [91], can be formed.

Table 5.3 shows the values of melting temperature and percentage of crystallinity obtained for the various composite products. In every case, the melting temperature stands at values slightly above 250 °C. The degree of crystallinity (X_c) was calculated considering the melting enthalpy (ΔH_m), the weight fraction of the glass fibers (%GF) and the theoretical melting enthalpy of a 100% crystalline material ($\Delta H_{m100\%}$) according the equation:

$$X_C = \frac{\Delta H_m}{\Delta H_{m100\%} \cdot (1 - \%GF)} \cdot 100 \quad (5.1)$$

As theoretical melting enthalpy of a 100% crystalline material was used a value of 199 J/g, obtained as an average of literature data [92–94].

Comparing the percentages of crystallinity between the reference material and the one at the end of life it is clear that natural aging, due to the use of the component, promotes the crystallization of the matrix. This effect is balanced by the thermomechanical degradation of the matrix due to recycling, in fact the remoulded products show a decrease in crystallinity degree. Probably the recycle steps determine the breakdown of the polymer chains with a consequent decrease in molecular weight and formation of smaller crystallites [53].

Table 5.3 Melting temperature T_m and degree of crystallinity X_c

Sample	T_m [°C]	X_c [%]
EoL	251,8	36,6
R	251,5	40,7
RM1	252,0	40,0
RM2	251,7	34,0
Ref	252,8	33,9

Figure 5.4 shows the X-ray diffraction patterns of virgin, end-of-life and recycled composites. All the spectra exhibit a broad hump in 2 theta region from 15° to 30° indicating that samples contain a portion of highly disordered material, which correspond to the amorphous component of semicrystalline PA6,6 matrix. The spectra of all investigated samples are comparable; the two main diffraction peaks at 2theta of 20,45° and 23,26° are distinctive of the α-crystal form of PA66. They are designed as α1 and α2 and correspond to (200) plane and (002)/(202) planes respectively [95,96]. As reported by Sanatgar et al. [97] the α_1 peak derives from the distance between the hydrogen-bonded chains, while the α_2 peak arises from the separation of the hydrogen-bonded sheets. A less intense peak at 2 theta of 25,28° is evident in XRD spectra of end-of-life and all recycled materials. This peak is characteristic of the quartz phase and for this reason is related to the glass fibers.

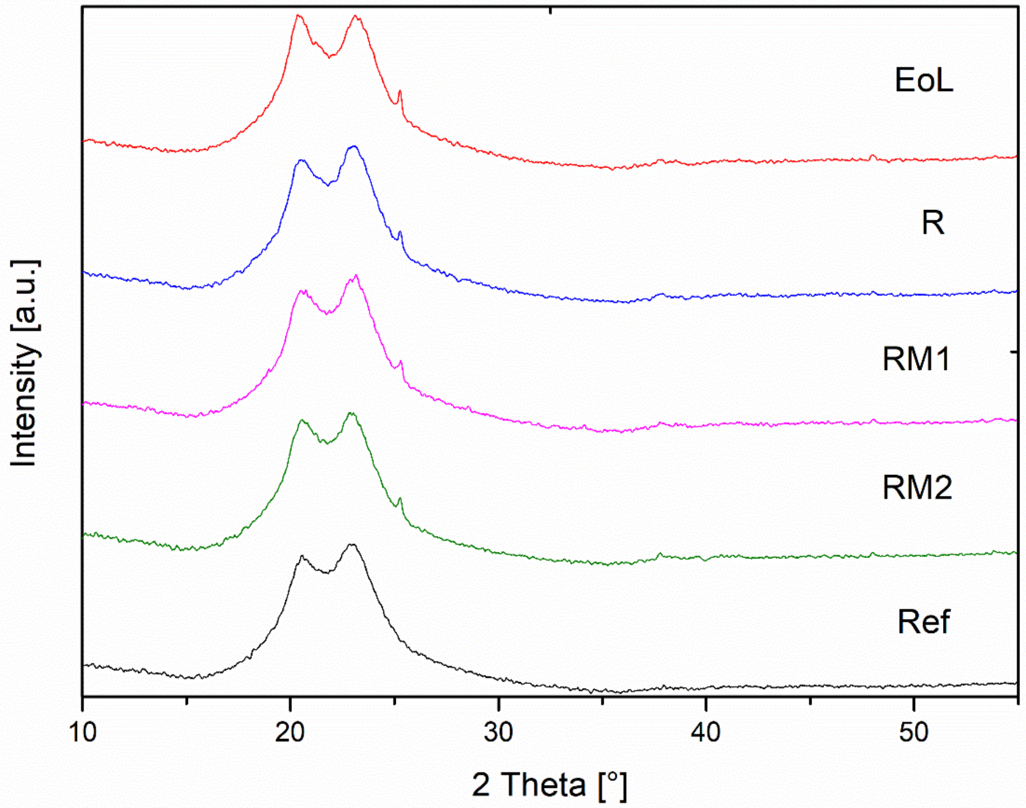


Figure 5.4 XRD spectra of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composite (Ref)

6.2 Microstructure and rheological characterization

The analysis of the effect of mechanical recycling on the length of the fibers was carried out by recovering the fibers after burning the matrix in an oven at 700 °C for each type of composite. The fibers thus obtained were placed on a glass slide and analysed with an optical microscope.

The figures 5.5, 5.6 e 5.7 respectively show the glass fibers taken from the end of life, the recycled and the remoulded products. For each type of fiber, approximately 200 fiber length measurements were collected in order to obtain statically significant values.

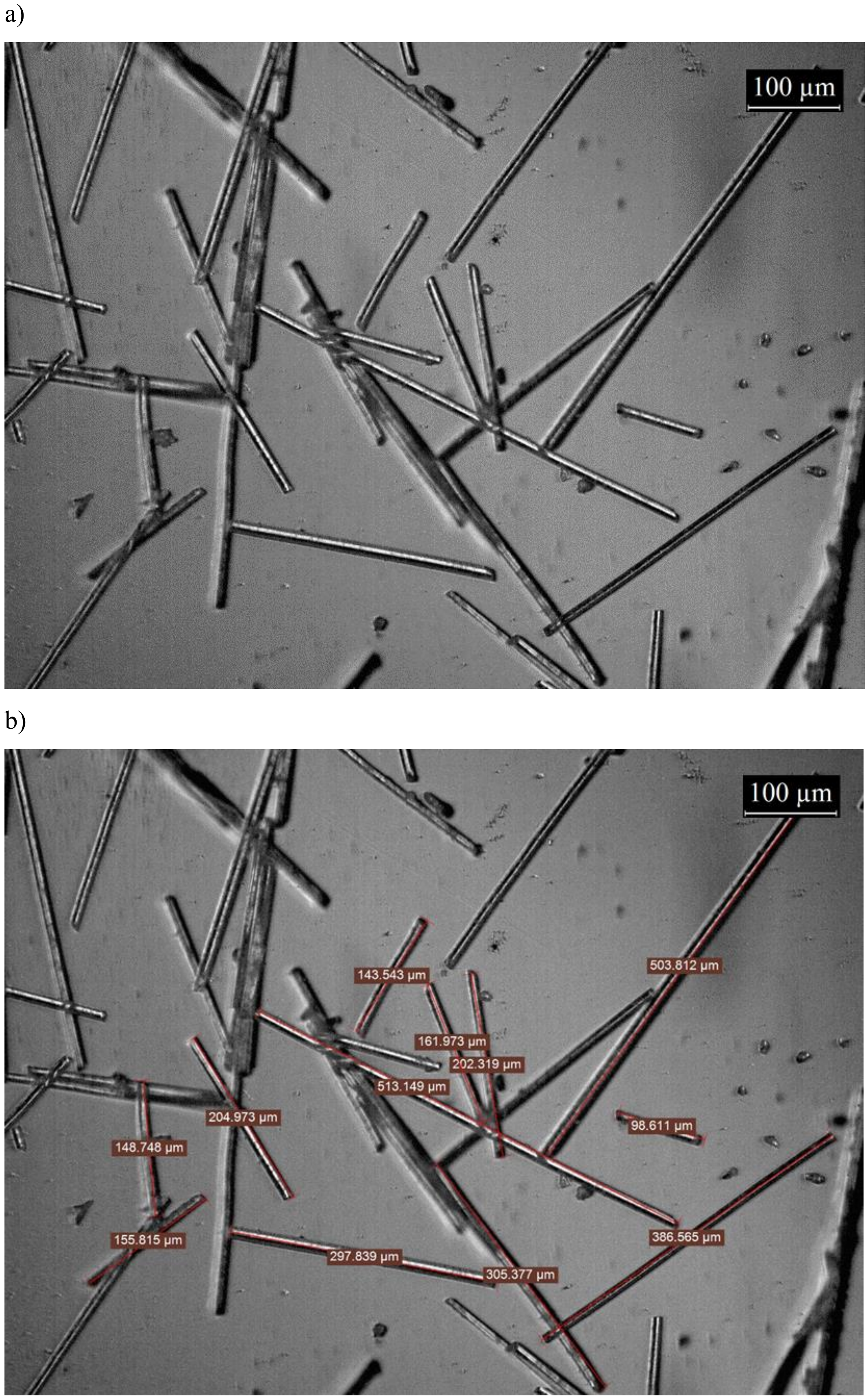


Figure 5.5 Fibers from the product EoL at 100x magnification under optical microscope in a) and measurement of fiber length in b)

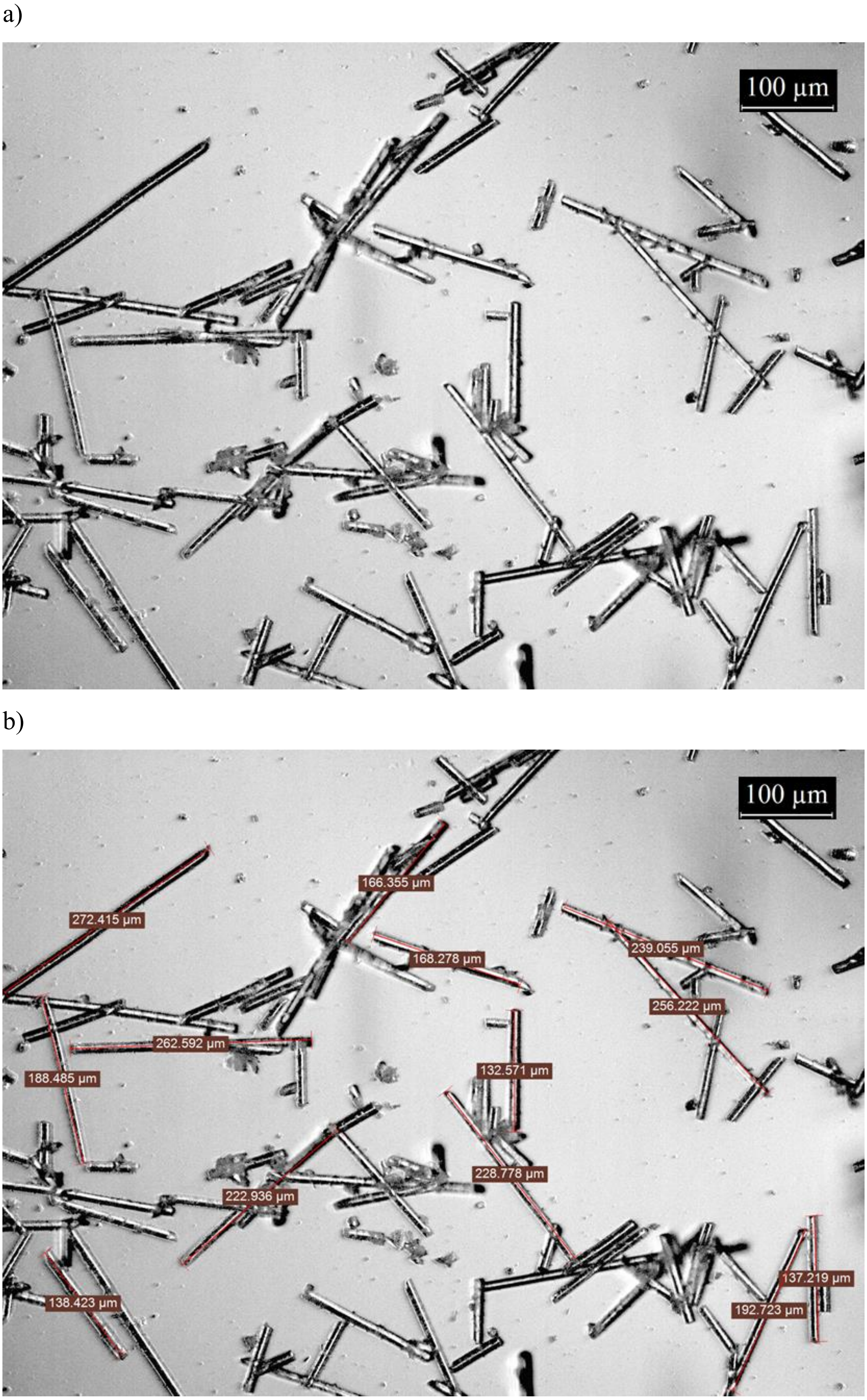


Figure 5.6 Fibers from the product R at 100x magnification under optical microscope in a) and measurement of fiber length in b)

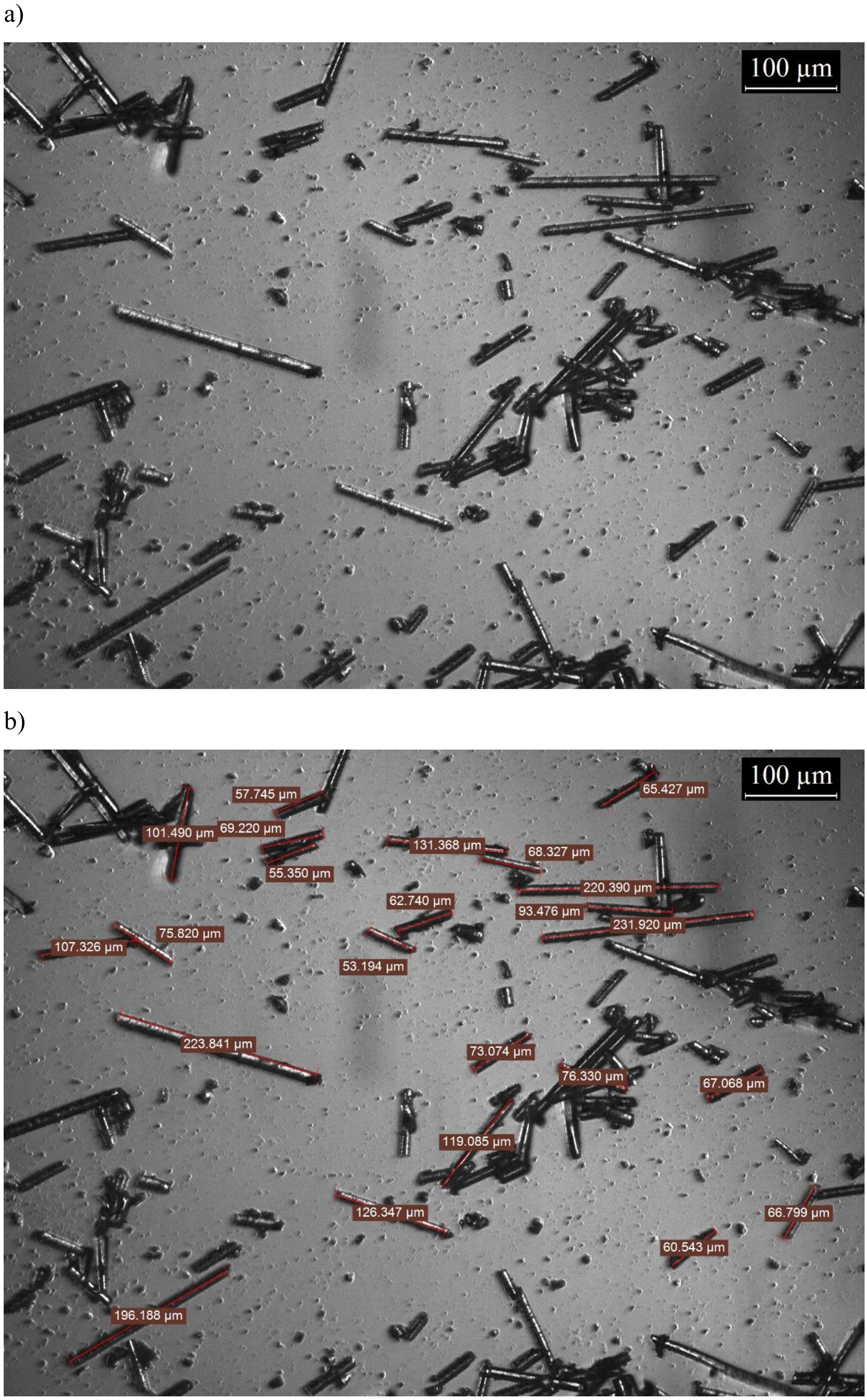


Figure 5.7 Fibers from the product RM1 at 100x magnification under optical microscope in a) and measurement of fiber length in b)

Table 5.4 and Figure 5.8 show the results of the fiber length analysis in terms of average values.

The reference material has an average fiber length of about 350 µm, while the end of life product has shorter fibers in the order of 250 µm. The difference in length of the fibers between the end-of-life and reference products is mainly due to the fact that the two materials are not exactly the same type of composite and therefore have different initial fiber length. To a lesser extent this difference in length is due to the mechanical degradation that occurs in the production of the component.

The difference in the initial length of the fibers between the reference material and the end of life component must be taken into consideration when comparing the mechanical properties of the materials.

As regards the other composite products, it is clear that as the number of recycling steps increases, the average length of the fibers decreases due to the breakage of the fibers that occurs during the processing steps. In fact, the average length drops to 175 µm for the recycled product, to 150 µm for the material reprocessed once, up to 124 µm for the composite reprocessed twice.

Table 5.4 Average fiber length for end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref).

Sample	Average fiber length (µm)
EoL	253 ± 107
R	175 ± 87
RM1	152 ± 87
RM2	124 ± 65
Ref	344 ± 219

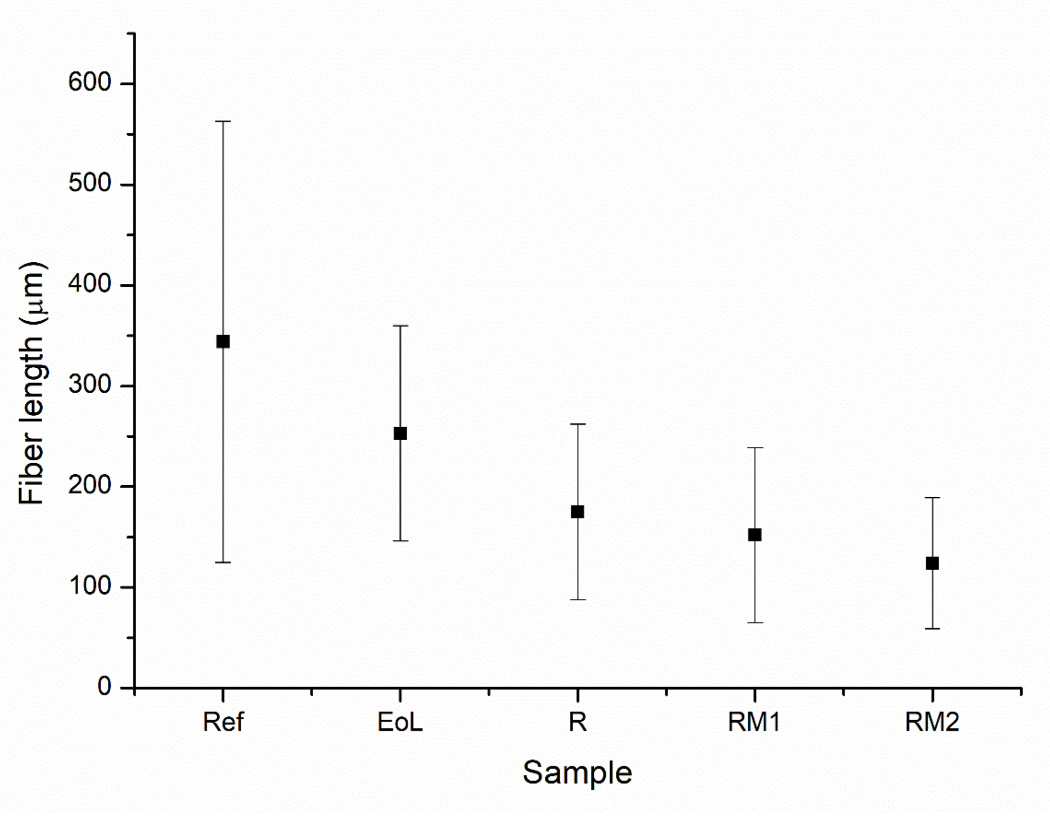


Figure 5.8 Average fiber length value and their standard deviations for each composite sample

Further considerations can be made by analysing the fiber length distribution of the different composite products. In the Figure 5.9 it can be seen how the reference material and the end of life composite have a pseudo Gaussian distribution, with a prevalence of fibers around 200-300 μm. Instead, the recycled product shows a distribution with a high number of fibers with dimensions below 100 μm compared to reference and end-of -life distributions. In the same way, fibers with size greater than 200 μm begin to decrease considerably for the R material. In fact, due to the recycling steps, the longer fibers are those that break more easily, causing this shift of the distribution towards smaller length values. As the number of reprocesses increases, the length of the fibers decreases, until it becomes increasingly difficult to break the short fibers. This effect is evident for RM1 and RM2 materials in which the distribution of fiber length is very similar, narrow and shifted to very low values. In fact, for the remoulded product more than 60% of the fibers have a length less than 100 μm.

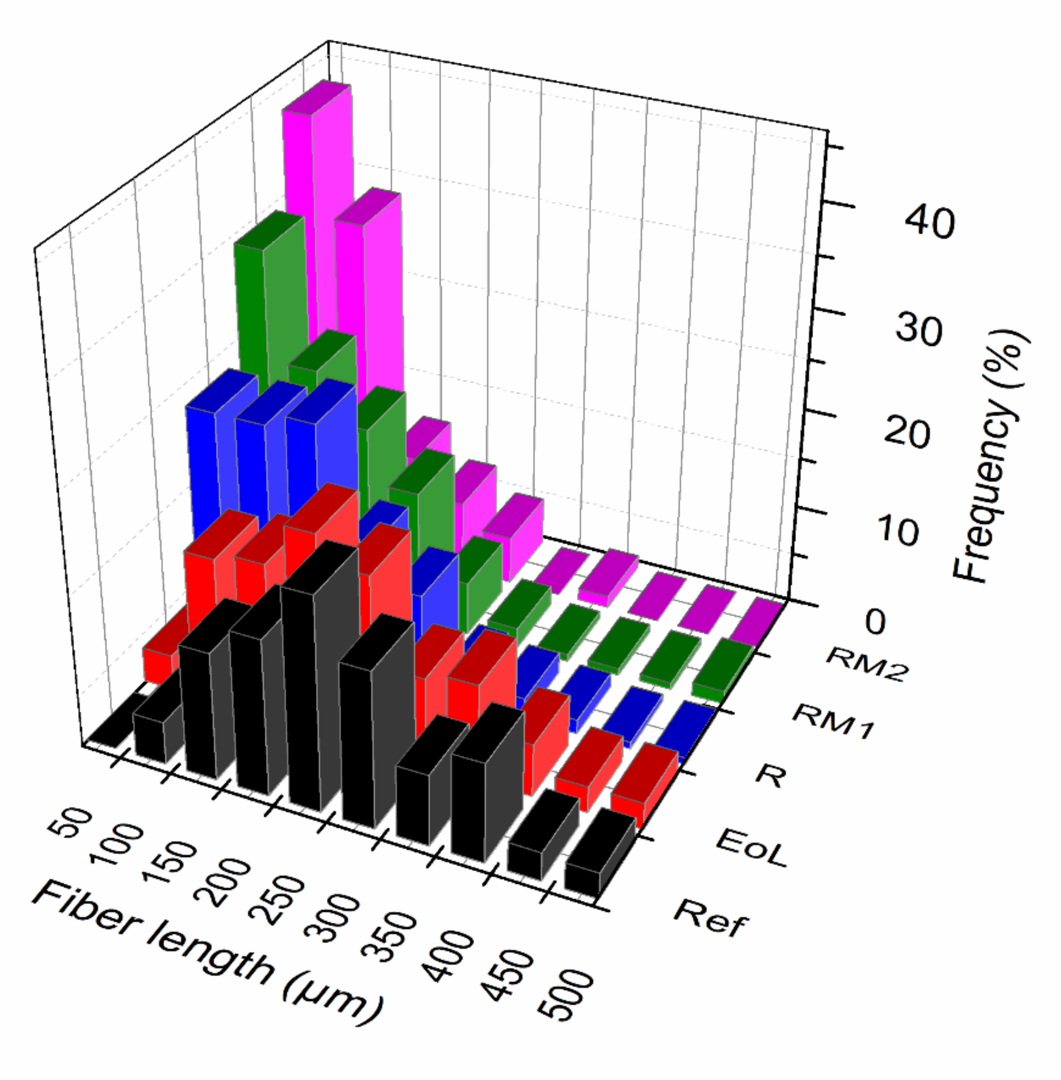


Figure 5.9 Fiber length distribution of end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref). For each length range the frequency is normalized and expressed as a percentage.

The rheological test in figure 5.10 shows the typical pseudoplastic trend for all the composite materials analysed, with a decrease in viscosity as the shear rate increases. Comparing the rheological curves between the reference material and the end of life component it can be noted that there is a viscosity drop of an order of magnitude. This fall can be associated with the degradation that the matrix undergoes during the years in which the component is in operation.

By mechanically recycling the material, the viscosity continues to decrease but with different trends. In fact, between the end of life component and the recycled R product there is a small difference in viscosity, while for the reprocessed products there is a further drop of an order of magnitude.

In addition to further degradation of the matrix, the decrease in viscosity as the number of recycling steps increases can be associated to the breakage of the fibers as shown in the analysis on their length. In fact, the rheological behaviour of composite materials is influenced not only by the percentage content of reinforcing phase, which in this case is almost the same for all products, but also by the length of the fibers [98,99].

In addition to the length of the single fiber, the interaction effect between one fiber and another must be taken into consideration. As fiber length increases, the entanglements between one fiber and the other increase until the formation of a percolation rheological network occurs, which hinders the mobility of the polymer chains, causing an increase in viscosity [100].

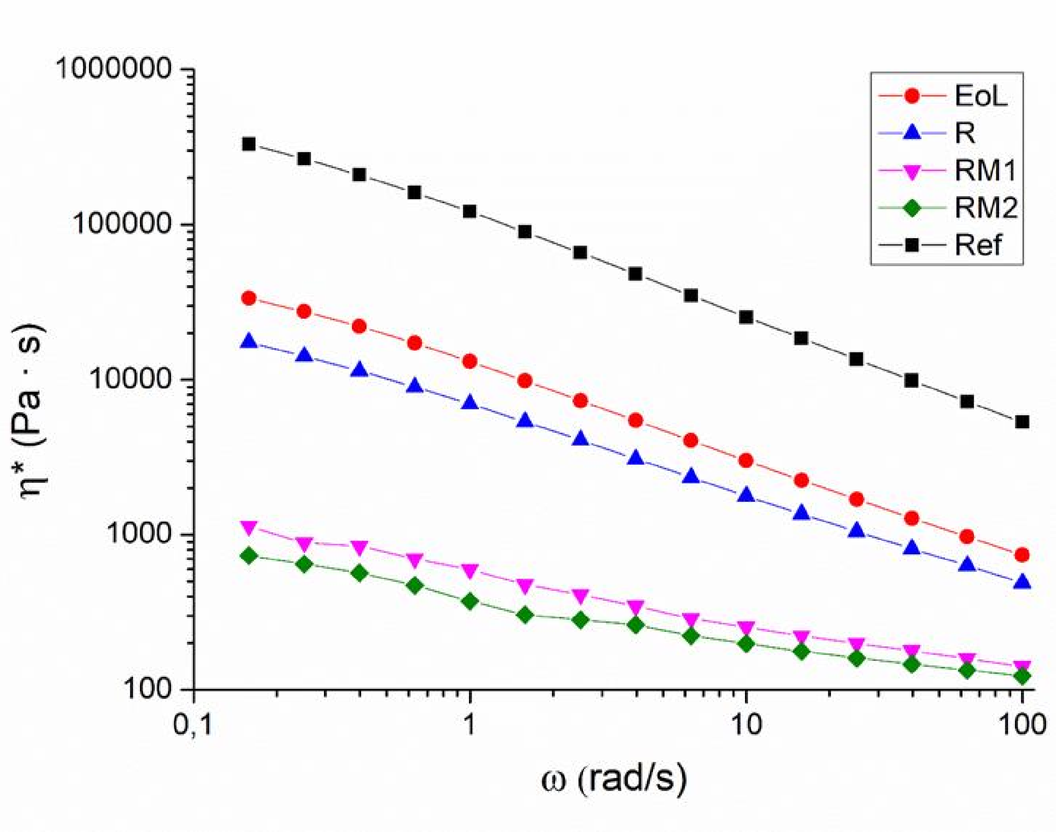


Figure 5.10 Complex viscosity measurements for end-of-life (EoL), recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

Comparing the results obtained from the rheological test with those concerning the fiber length distribution, it can be stated that the fibers of the EoL and R products have a sufficient length to guarantee the formation of the percolation rheological network. The reprocessed products instead have a considerable percentage of fibers under 100 μm and almost no fiber over 300 μm in length. This suggests that the system for this two products is below the percolation threshold with consequent strong drop in viscosity [101]. Once the network has been lost, it becomes increasingly difficult to further break the short fibers, and therefore there is a small difference in viscosity between RM1 and RM2 materials.

The tensile specimens obtained for the R, RM1 and RM2 composites were sectioned in the direction perpendicular to the specimen axis and observed under an optical microscope to analyse orientation and distribution of glass fibers.

Figure 5.11 shows an example of the images taken under the optical microscope at different magnifications. The images show a good dispersion of the fibers in the matrix and absence of porosity. The fibers have a diameter of around 10 μm and are almost all aligned in the moulding direction.

The high orientation of the fibers in the injection direction is confirmed by processing the images with the Matlab program described in paragraph 4.6 of the previous chapter. The results of the Matlab analysis in Figure 5.12 and Table 5.5 allow to assess fiber average orientation angles of 3° for all the three composite products. Therefore, the decrease in fiber length with increasing recycle steps does not affect the orientation of the fibers during the injection moulding.

Table 5.5 Fiber average orientation angle θ, with respect to the injection direction and the tensile specimen axis, of recycled (R) and remoulded samples (RM1, RM2)

Sample	θ
R	3,11°
RM1	3,74°
RM2	3,14°

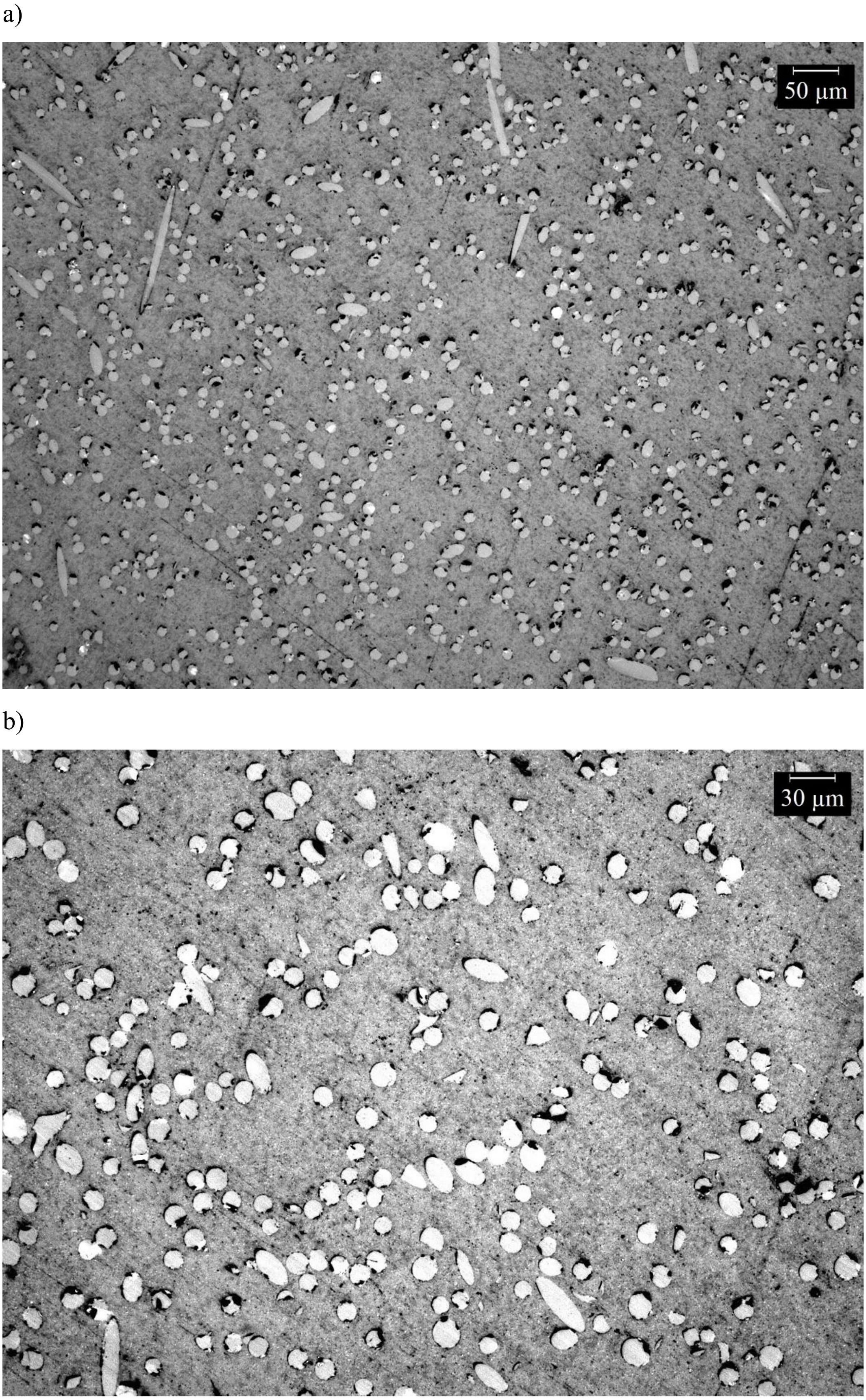


Figure 5.11 Optical micrographs of the section of the composite at different magnification (a) 100X, (b) 200X.

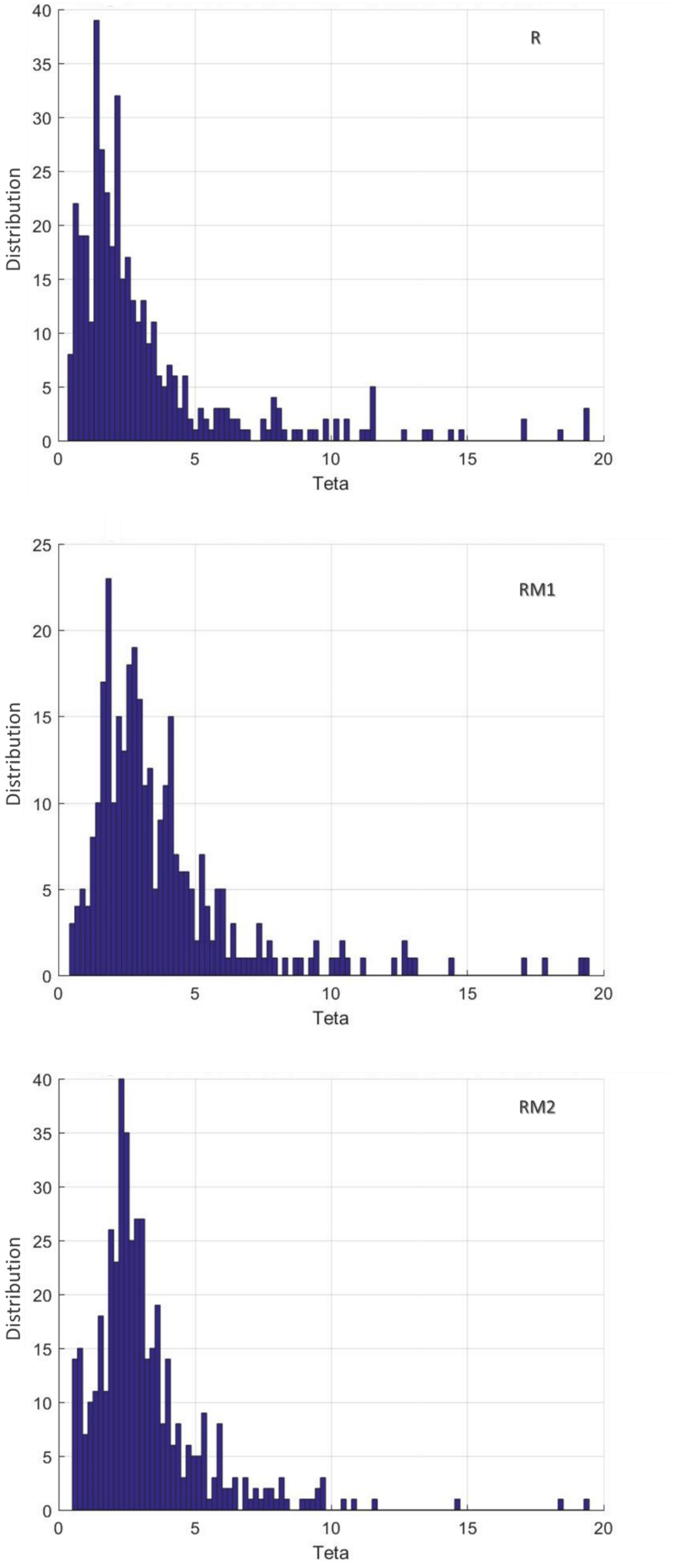


Figure 5.12 Histograms of the orientation of the fibers in the angle range 0-20° of recycled (R) and remoulded samples (RM1, RM2)

6.3 Mechanical tests

The effect of recycling on the mechanical properties of the end of life component has been analysed by tensile and bending tests on the samples obtained by injection moulding both for the three different reprocessed products (R, RM1, RM2) and for the reference material (Ref).

Figure 5.12 shows for each product the most representative curves of the tensile tests, as they are more similar to the average of the values obtained.

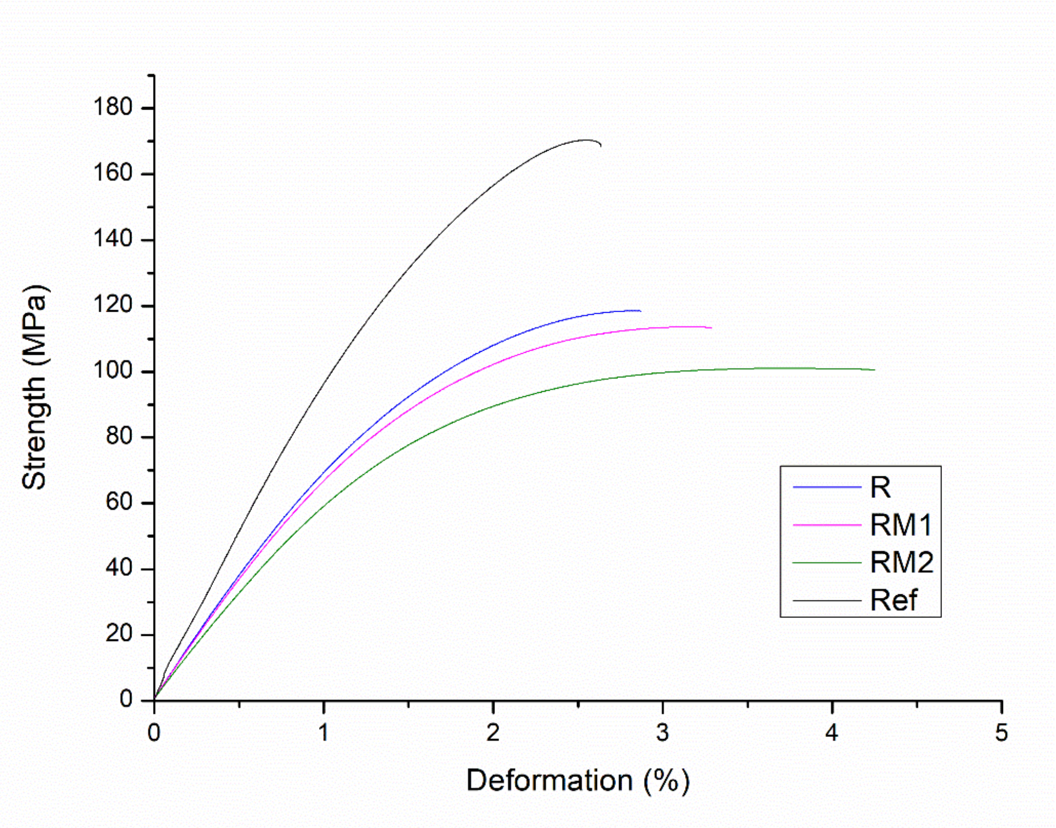


Figure 5.13 Representative tensile curves obtained for recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

Table 5.6 shows the tensile test results obtained in terms of modulus, strength and deformation for the different composite materials. In general, the trend shows that there is a worsening both of the elastic modulus and of the tensile strength, while the elongation at break increases after recycling processes. The major difference concerns the comparison between reference material (Ref) and recycled product (R). This is what was expected, since the end-of-life component has undergone natural aging during its use, in addition to the grinding and injection moulding processes.

Table 5.6 Tensile test results of PA66GF Composites (R, RM1, RM2, Ref) compared to unreinforced (UR) PA66 mechanical properties

Sample	Elastic modulus [GPa]	Tensile Strength [MPa]	Deformation [%]
R	7,8 ± 0,3	120,0 ± 2,3	3,0 ± 0,3
RM1	7,4 ± 0,1	113,5 ± 0,2	3,4 ± 0,1
RM2	6,7 ± 0,2	100,8 ± 1,3	4,2 ± 0,3
Ref	10,2 ± 0,5	170,5 ± 5,2	2,6 ± 0,1
UR	2,05	55	7

In detail, after recycling and in comparison with the reference material, there is a 29% resistance drop from 170 MPa to 120 MPa and a 23% decrease in the Young modulus from 10.2 GPa to 7.8 GPa. This difference in mechanical properties, in addition to the degradation suffered by the material, must be associated with the different initial length of the fibers. In fact, the reference material has an average fiber length of 344 μm, while the end-of-life component of 250 μm only, which goes down to 175 μm after the first recycling step.

Halving the average fiber length between the reference material and the recycled one has a noticeable effect on the capability of the fibers to reinforce the matrix. According to the shear-lag model, the effectiveness of the load transfer from the matrix to the short fibers depends on the length of the fibers. This is because the end part of the fiber is not able to completely support the load and therefore, as the length of the fiber increases, the part able to completely transfer the load increases. When the length of the fiber goes below a certain critical value, no part of the fiber completely transfers the load with a worsening of the reinforcing effect. According to literature data, it can be stated that the reference composite has fiber lengths higher than the critical value while recycled products are below the critical length [102].

Reprocessing the recycled material two more times the decrease in strength and modulus is lower. In particular, the resistance decreases by 16% from the product R to RM1 and by 11% from RM1 to RM2. These results agree with Bernasconi et al. work reported in paragraph 2.3 in which, by 100% reprocessing a polyamide 66 reinforced with 35% glass fibers, an 11% decrease in tensile strength was found.

Despite the worsening of mechanical properties, recycled products always grant higher modulus and tensile strength than the non-reinforced matrix. The last line of Table 5.6 shows the mechanical properties of a unreinforced polyamide 6,6 (UR) marketed by the same company as the reference material with the name of Radilon A ESL128 [103]. The recycled component, even after the second remoulding has a module that is more than triple and tensile strength almost double of the non-reinforced material.

The results of the bending tests in Figure 5.13 and table 5.7 show the same trend as the tensile tests. Between the reference material and the recycled material there is a difference of 28% in strength and 24% in modulus, while the deformation at break remains at the same value. Instead, unlike the tensile tests, if the material is reprocessed twice more, the loss in bending properties is limited. The values between R and RM1 are almost the same, while between RM1 and RM2 the decrease in strength and elastic modulus is 8%. The deformation at break instead increases by 1% and 1.5% between R and the remoulded products.

Table 5.7 Bending test results of PA66GF Composites

Sample	Elastic modulus [GPa]	Bending Strength [MPa]	Deformation [%]
R	6,83 ± 0,13	187,7 ± 7,4	3,7 ± 0,3
RM1	6,42 ± 0,04	186,5 ± 1,4	4,7 ± 0,2
RM2	5,87 ± 0,06	171,3 ± 2,5	5,2 ± 0,4
Ref	9,03 ± 0,33	263,6 ± 8,9	3,7 ± 0,1

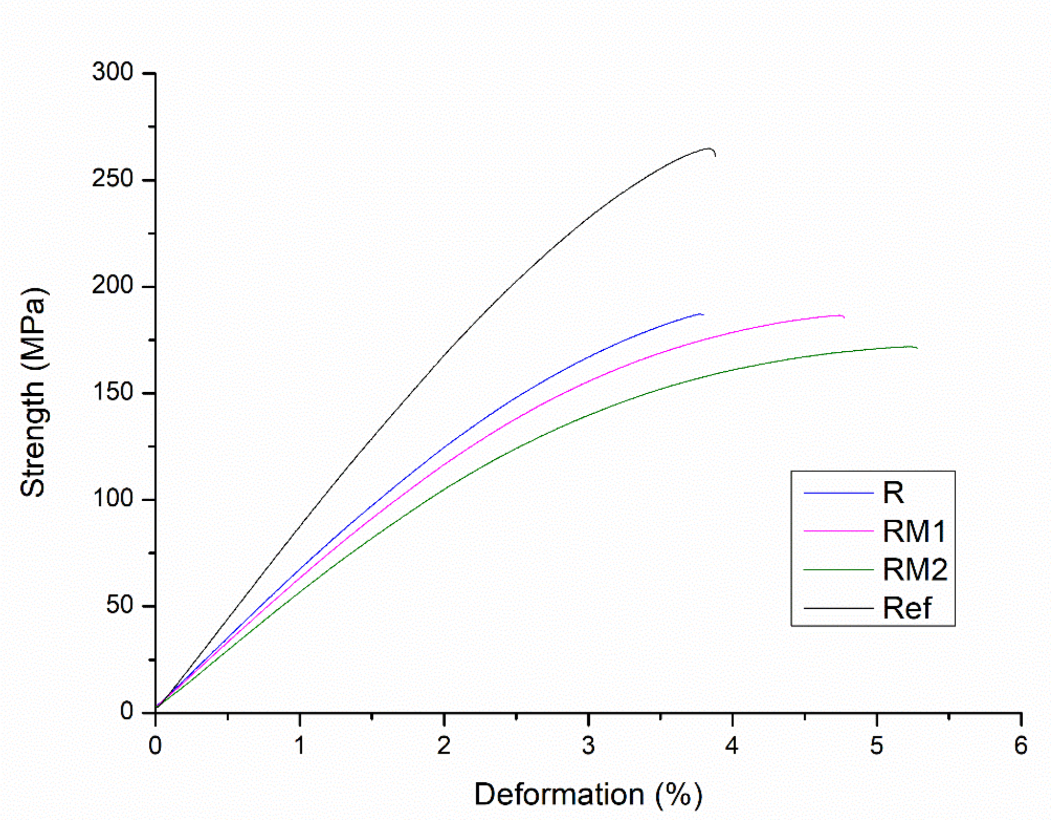


Figure 5.14 Representative bending curves obtained for recycled (R), remoulded (RM1, RM2) and reference composites (Ref)

5.4 Conclusions

In this work the possibility of mechanically recycling an automotive composite component at the end of its life was investigated. The component is a radiator cooling system made of polyamide 6,6 reinforce with 35% of glass fibers coming from waste currently landfilled.

The mechanical recycling process, repeated three times, involves crushing, pelletizing and injection moulding operations. The recycled end-of-life material was compared with a composite of the same type in polyamide 6,6 reinforced with the same percentage of fibers but showing different fiber length.

Mechanical recycling determines a decrease in fiber length, while it has no effect on the orientation of the fibers, which for all three recycling stages remain strongly oriented in the injection direction. The decrease in fiber length affects both the rheological and mechanical properties.

The degradation of the composite due to its operational use causes the first drop in viscosity with respect to the reference material, while the difference in viscosity between recycled product and further remoulded ones is correlated to the loss of the rheological percolative network.

The end-of-life component recycled mechanically has worse mechanical properties than the non-aged reference material. The worsening in mechanical properties due to matrix degradation and fiber length reduction becomes less evident in further recycling treatments as it is increasingly difficult to break again short fibers. The recycled materials always display higher mechanical properties than the same non-reinforced matrix.

In conclusion the results achieved suggest the use of the recycled material in the automotive sector for components currently produced with PA6 reinforced up to 15% in glass fiber or not reinforced such as carbon canisters, connectors, fasteners, headlight bezels and turbo air ducts [104].

Chapter 6

Mechanical recycling of processing scraps

In this research activity the possibility of mechanically recycling automotive composite processing scraps was investigated. The scraps consist of a laminate made of a polyamide 6 matrix reinforced with a twill-weave type textile of continuous glass fiber at 66% by weight.

For clarity, Table 6.1 shows the abbreviations used to indicate the different types of material.

Table 6.1 Abbreviations used to indicate the different types of material

Abbreviation	Material
CM-PA6-30GF	Compression moulded polyamide 6 reinforced with 30% glass fiber
CM-PA6-15GF	Compression moulded polyamide 6 reinforced with 15% glass fiber
CM-PA6	Compression moulded virgin polyamide 6
IM-PA6-15GF	Injection moulded polyamide 6 reinforced with 15% glass fiber
IM-PA6	Injection moulded virgin polyamide 6

6.1 Thermal and fiber length analysis

Since the laminate contains 66% by weight of glass fibers, after the grinding two blends were produced to reduce the amount of fibers to 30% and 15% using a virgin PA6. First, thermogravimetric analyses were carried out both in air and in argon on the starting laminate, on the virgin material and on the two products after mixing. In Figures 6.1 and 6.2 the curves in air and argon of the various products are reported. The curves show that the degradation occurs in a single step with a continuous weight fall, according to the mechanism of chain breakage with formation of radicals typical of polyamides [105].

Table 6.2 presents the amount of solid residues and the initial degradation temperature $T_{2\%}$ of the tested materials. From the analysis of the residues it can be understood if the mixing has been carried out correctly. In this case residues of 30% and 15% respectively were detected at the end of TGA test carried out in both atmospheres, thus confirming that the mixing of the ground laminate was carried out by adding the right amount of virgin material. As regards the initial temperature of degradation, which is conventionally defined as the temperature at which a weight loss of 2% occurs, the presence of fibers increases the thermal stability of the material with respect to the virgin one. In fact, the degradation temperature starts from 320 °C for the virgin PA6 in argon, it increases to 350 and 355 °C respectively for the products having 15% and 30% of glass fibers obtained after the first and the second mixing, and increases up to 375 °C for the laminate with 66% glass fiber. In conclusion, from the TGA results it can be stated that there are no substantial differences between oxidizing and inert atmosphere.

Table 6.2 Initial degradation temperature and residue of PA6GF composites and PA6 virgin material

Sample	Argon		Air	
	$T_{2\%}$ [°C]	Residue [%]	$T_{2\%}$ [°C]	Residue [%]
Laminate	375	66.9	378	64.8
1st mixing (30%)	355	30.23	357	30.15
2nd mixing (15%)	350	15.66	351	15.87
Virgin PA6	320	0.36	324	0.53

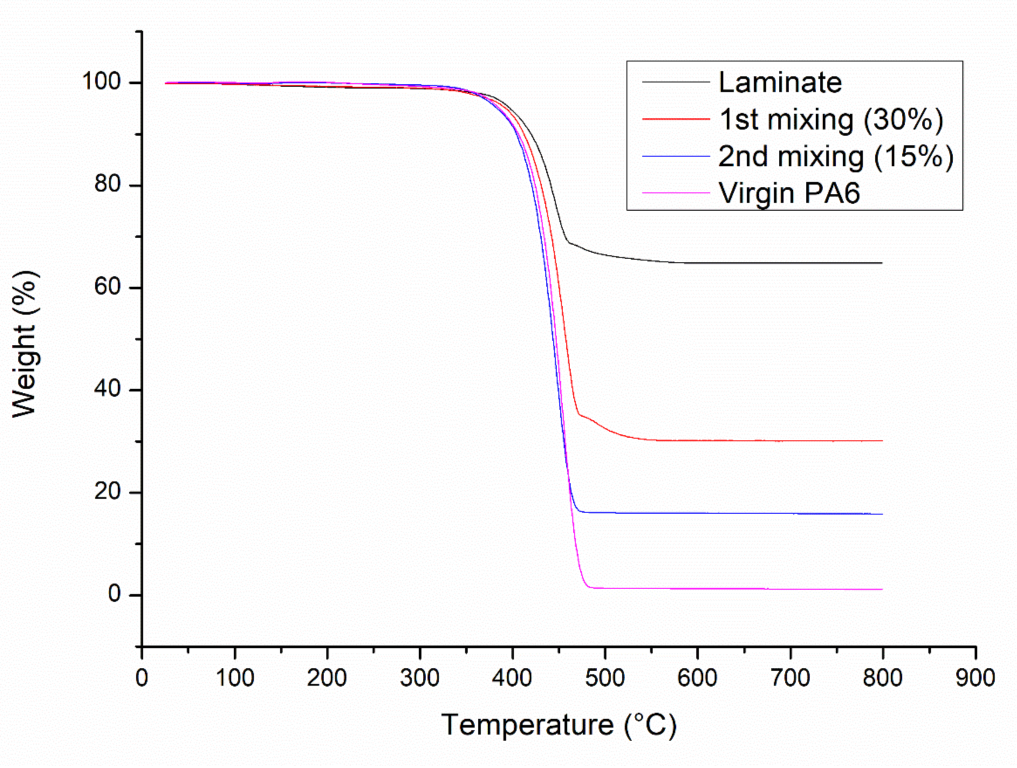


Figure 6.1 TGA analysis performed in air of PA6GF composites and PA6 virgin material

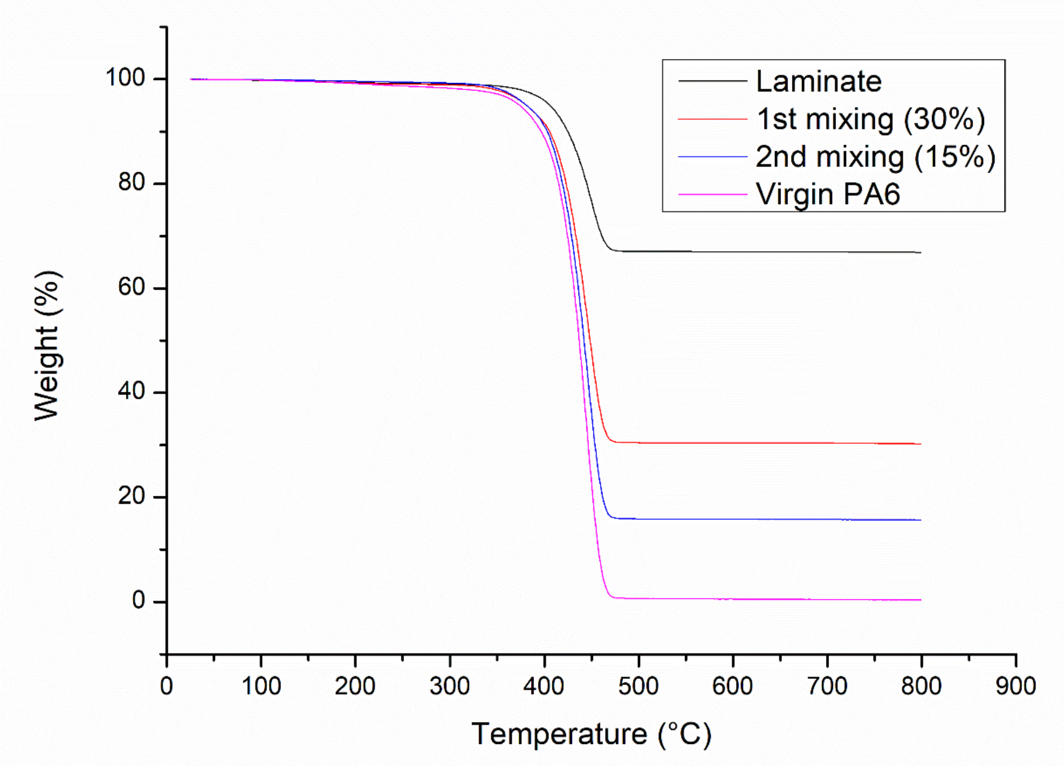


Figure 6.2 TGA analysis performed in argon of PA6GF composites and PA6 virgin material

The starting laminate was reinforced with a twill-weave fabric of long continuous glass fiber. Therefore, the grinding determines the breakage of the continuous fibers of the laminate and the obtaining of short glass fibers.

The fiber length analysis after grinding was carried out by burning the matrix at 700°C and analysing the obtained fibers under the optical microscope. Figure 6.3 illustrates the fiber length distribution obtained by measuring about two hundred fibers using the image processing software of the optical microscope. Figure 6.4 shows one of the images taken from the microscope in which it can be noted the presence of fibers of different lengths, but always greater than 300 µm.

The fiber length distribution shows that just over 40% of the fibers have a length between 500 and 600 µm, another 40% is less than 500 µm long, while the residual 20% is longer than 600 µm. Overall the average fiber length is 530 ± 124 µm.

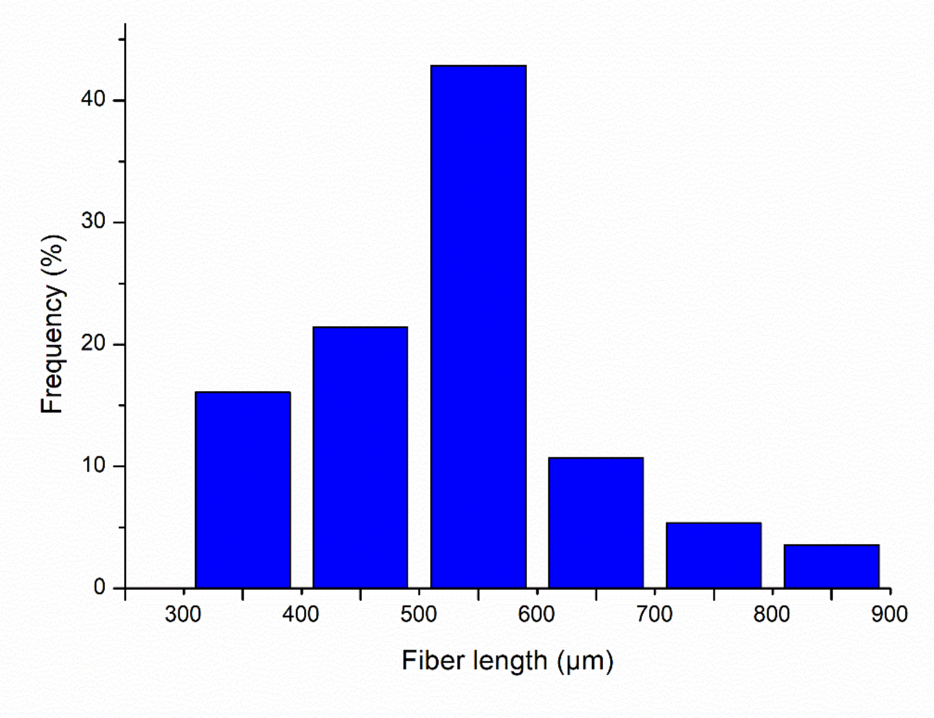


Figure 6.3 Fiber length distribution of manufacturing scraps after grinding

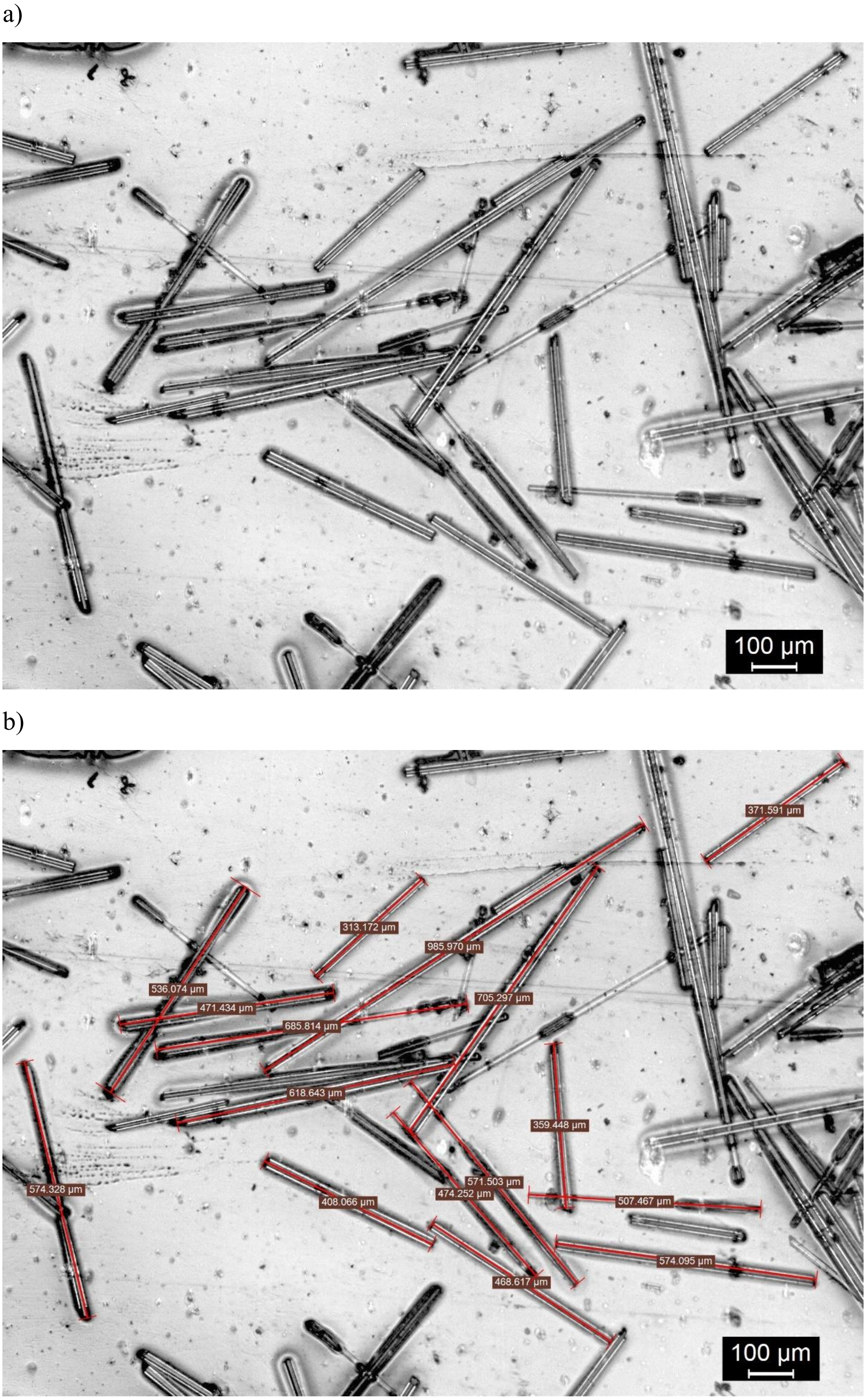


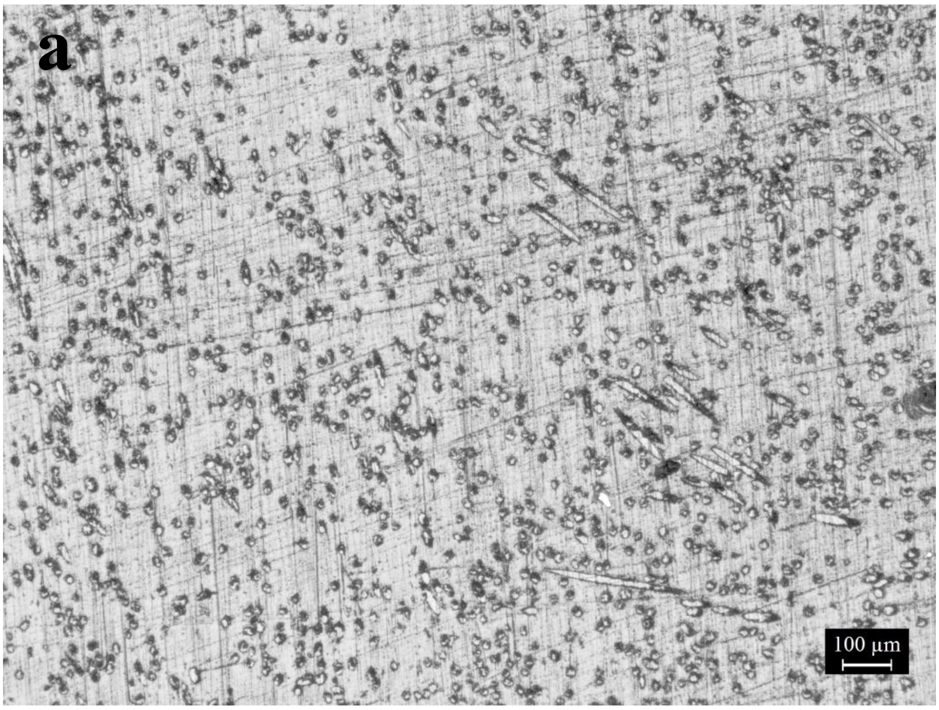
Figure 6.4 Fibers of manufacturing scraps after grinding at 50x magnification under optical microscope in a) and measurement of fiber length in b)

6.2 Microstructural and density characterization

The materials after mixing were processed by compression and injection moulding, but, as explained in paragraph 4.1, it was not possible to injection-mould the polyamide with 30% glass fibers. The specimens obtained were sectioned and observed by means of an optical microscope.

In the Figures 6.5, 6.6 and 6.7 it can be observed the effect that the two different technologies have on the microstructure of the composite. In the first images relating to the compression moulded composites a certain amount of fibers can be observed arranged parallel to the section plane. This is linked to the fact that compression moulding involves the filling of the mould with randomly oriented pellets. Even if the fibers with high orientation angles appear to be few, it must be considered that during polishing many fibers of this type tend to be mechanically removed. The images in Figure 6.7 regarding the injection moulded specimen show instead a high orientation of the fibers in the injection direction. Furthermore, the fibers have a diameter around 20 μm (Figure 6.7 c).

Another substantial difference between the two forming technologies concerns the presence of porosity which affects the density of the material. In the compression moulded specimens, porosities in the range of 50-100 μm can be observed (Figure 6.5 b and Figure 6.6 a). On the contrary, porosity is not visible in the micrographs of the injection moulded sample.



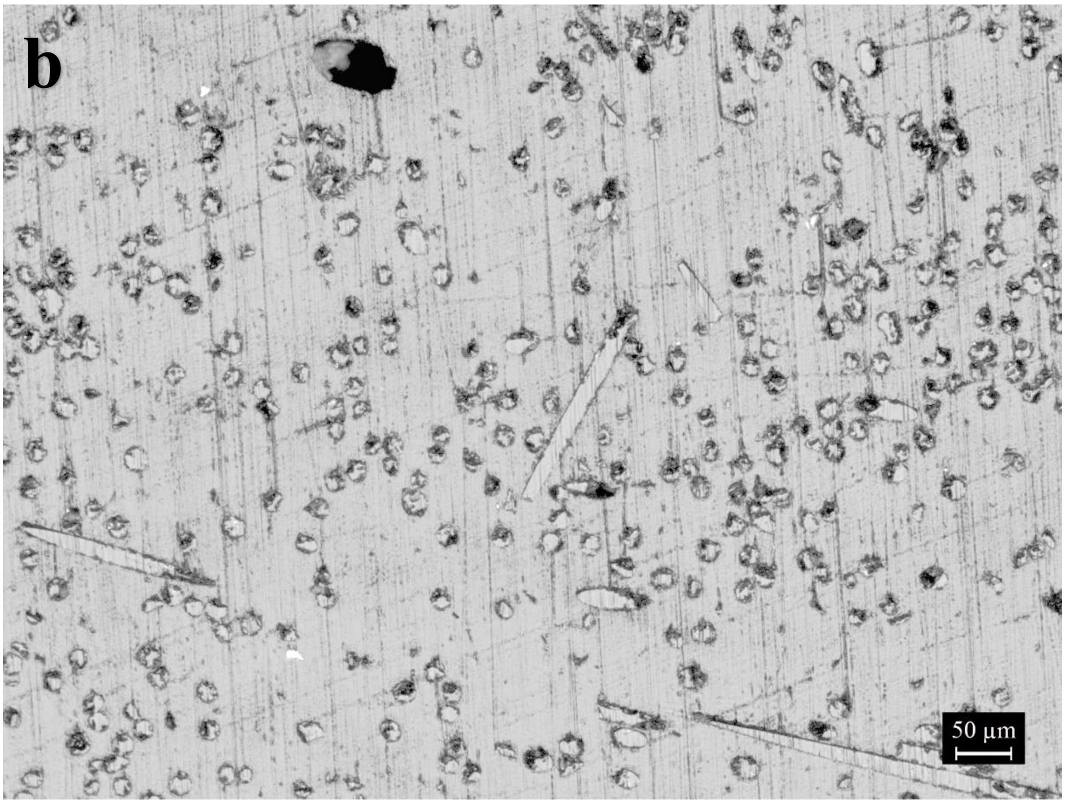


Figure 6.5 Optical micrographs of the section of the CM-PA6-30GF composite at different magnification (a) 50X, (b) 100X.

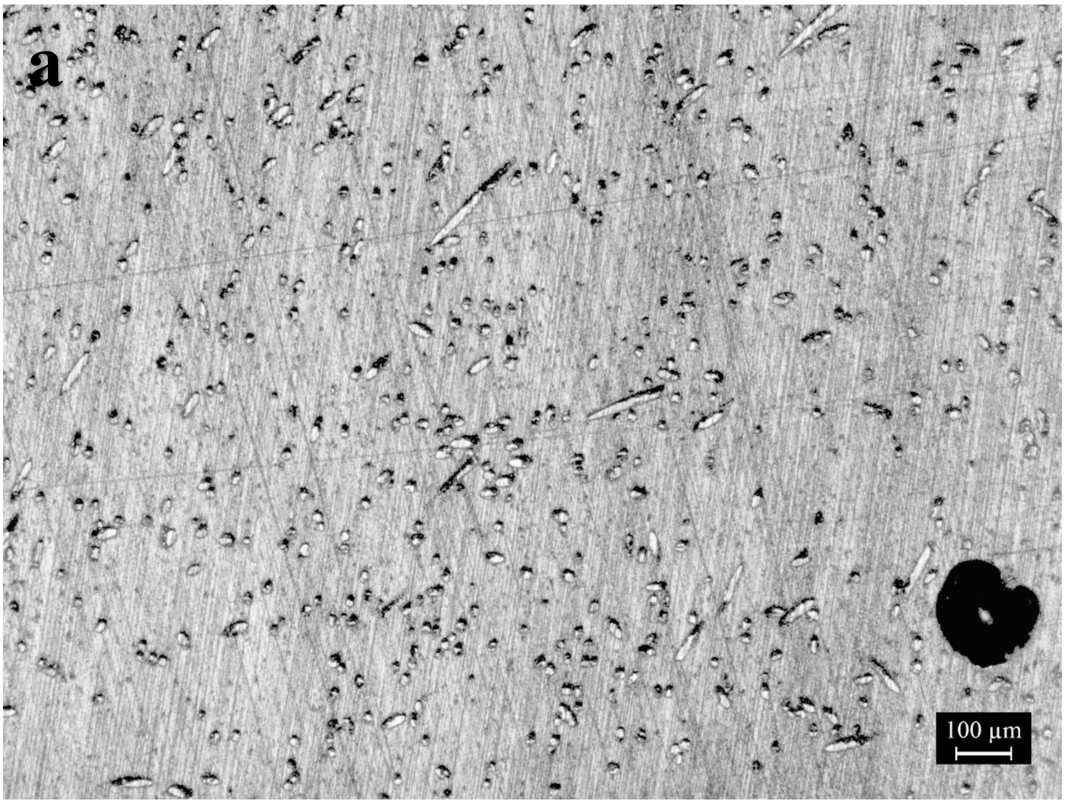
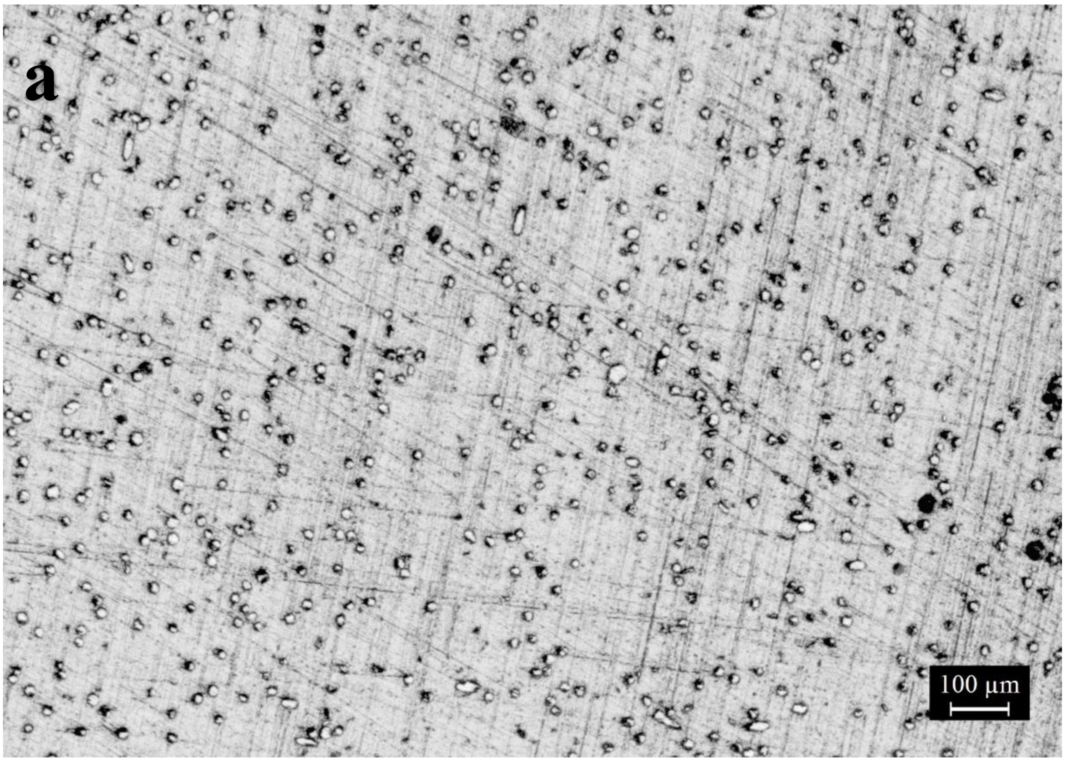


Figure 6.6 Optical micrographs of the section of the CM-PA6-15GF composite at different magnification (a) 50X, (b) 100X.



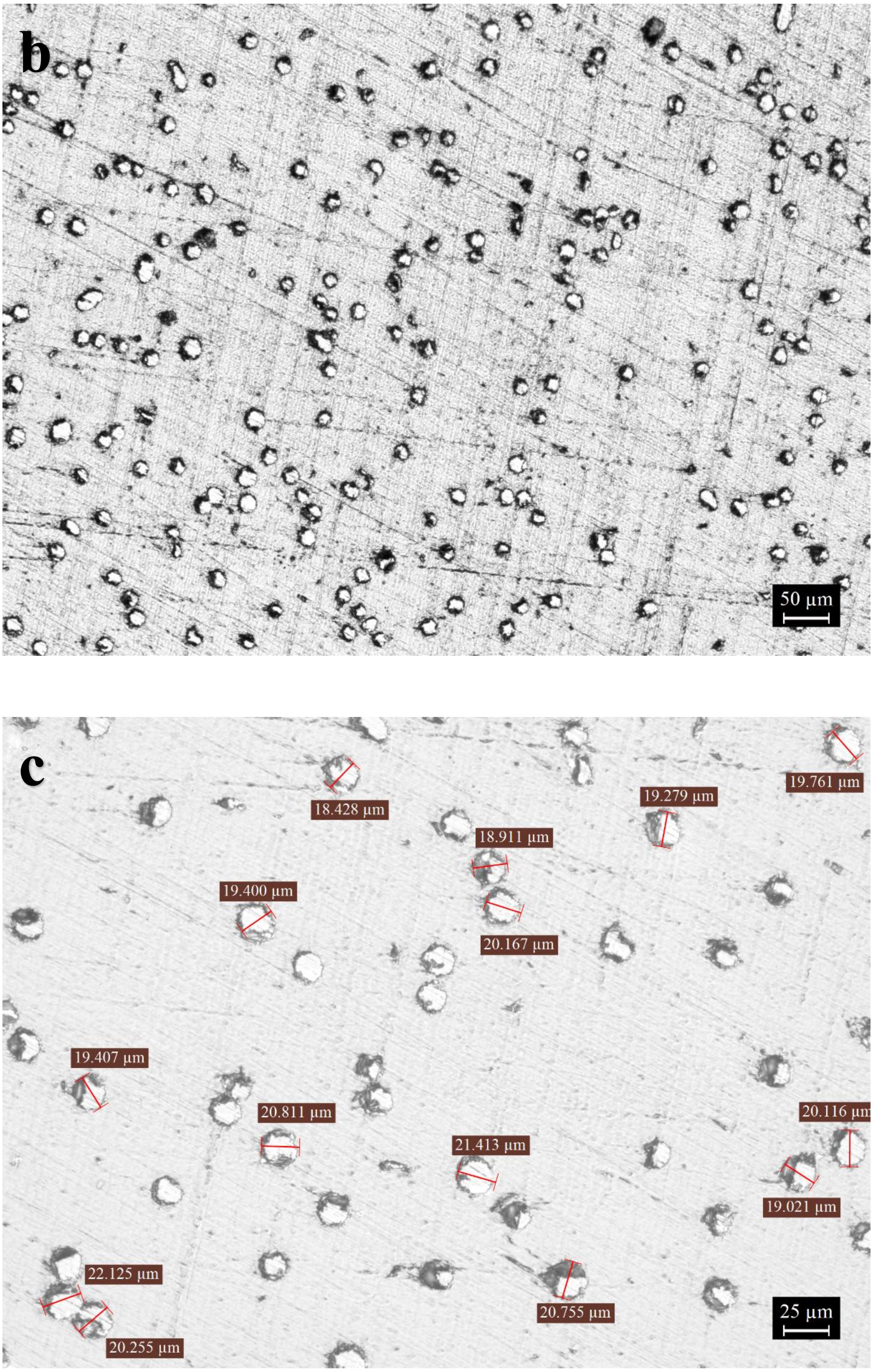


Figure 6.7 Optical micrographs of the section of the IM-PA6-15GF composite at different magnification (a) 50X, (b) 100X (c) 200X

The presence of porosities observed with the optical microscope was confirmed by the density measurements performed on the samples. The density measurements results were compared to the theoretical density in order to evaluate the relative density of the sample. Table 6.3 illustrates that compression-moulded glass fiber products have a relative density of 96% and 95%. The density measurements show that only the injection-moulded material has a density equal to the theoretical value.

The decrease in relative density can be attributed to the effect of the moulding technology, since the strong pressures involved in injection moulding reduce the presence of porosity in the final product. Conversely, in compression moulding the degassing phase is fundamental after the material has been heated, as the air present between the pellets can be trapped in the sample and gives rise to porosity as shown in the optical microscope images.

Table 6.3 Density measurements of PA6GF composites and PA6 virgin material

Sample	**Relative density**	
	Compression	Injection
PA6	97,5 %	99,8 %
PA6-15GF	96,0 %	99,7 %
PA6-30GF	95,1 %	-

6.3 Mechanical tests

The specimens obtained by compression and injection moulding of both the virgin and the reinforced material were submitted to tensile tests.

Figures 6.8 and 6.9 show the representative curves of each set of samples. The selected curve is the one that best describes the average values of properties shown in Table 6.4.

From the comparison between the injection moulded and compression moulded virgin material it can be seen how the kind of moulding process affects the final mechanical properties of the samples. The main differences concern tensile strength and deformation. IM-PA6 has a tensile strength of 68.5 MPa which drops to 43.1 MPa for CM-PA6 with a decrease of 37%, while deformation at break reduces by eight times from 32% to 4%. The decrease of the young module is much more contained instead (11%), going from 2.78 GPa for the injection samples to 2.47 GPa for the compression ones.

Table 6.4 Tensile test results of injection moulded (IM) and compression moulded (CM) samples

Sample	Elastic modulus [GPa]	Tensile Strength [MPa]	Deformation at break [%]
IM-PA6	2,78 ± 0,09	68,5 ± 0,1	32,1 ± 6,4
IM-PA6-15GF	4,81 ± 0,09	74,4 ± 1,2	2,2 ± 0,1
CM-PA6	2,47 ± 0,33	43,1 ± 4,6	4,2 ± 1,1
CM-PA6-15GF	4,01 ± 0,41	29,6 ± 5,1	0,8 ± 0,1
CM-PA6-30GF	5,19 ± 0,32	45,2 ± 6,7	1,0 ± 0,2

The injection-moulded recycled material with 15% glass fibers has better mechanical properties than the virgin equivalent. The module increases by 73% thanks to the presence of fibers, reaching values of 4.81 GPa. As regards tensile strength values, it must be considered that the virgin and reinforced injection moulded samples have different tensile behaviour. The curves in Figure 6.9 highlight the plastic behaviour of the virgin material and the brittle behaviour of the composite samples. The values shown in the Table 6.4 refer to the maximum strength of the material which in the case of the reinforced sample coincides with the yield point, while for the virgin material yield strength and tensile strength differ significantly. In fact, the maximum resistance for the virgin material is equal to 68.5 MPa, and it is obtained at a deformation of 20%, while the yield point is set at 50 MPa. Therefore, comparing the maximum strength values of the injection moulded material shown in table 6.4 it can be concluded that this last material shows a 9% increase in resistance, while if the yield values are considered, the increase is 50%.

As far as the compression moulded samples are considered, the reference values of the virgin material are 2.5 GPa of modulus and 43 MPa of tensile strength. As regards the module, the presence of the 15% or 30% of reinforcing phase increases the material's stiffness by 60% and 110% respectively with respect to the unreinforced samples.

The CM-PA6-15GF sample shows a lower tensile strength than compression moulded unreinforced polyamide. Increasing the fiber content to 30% it is possible to obtain tensile strength values equal to those of the non-reinforced material also with compression moulding.

In general, it should be emphasized that the tensile strength values for compression moulded specimens show a greater standard deviation than those obtained for injection moulded samples. This is mainly due to the presence of porosity connected to the technological process which affects the reproducibility of the data.

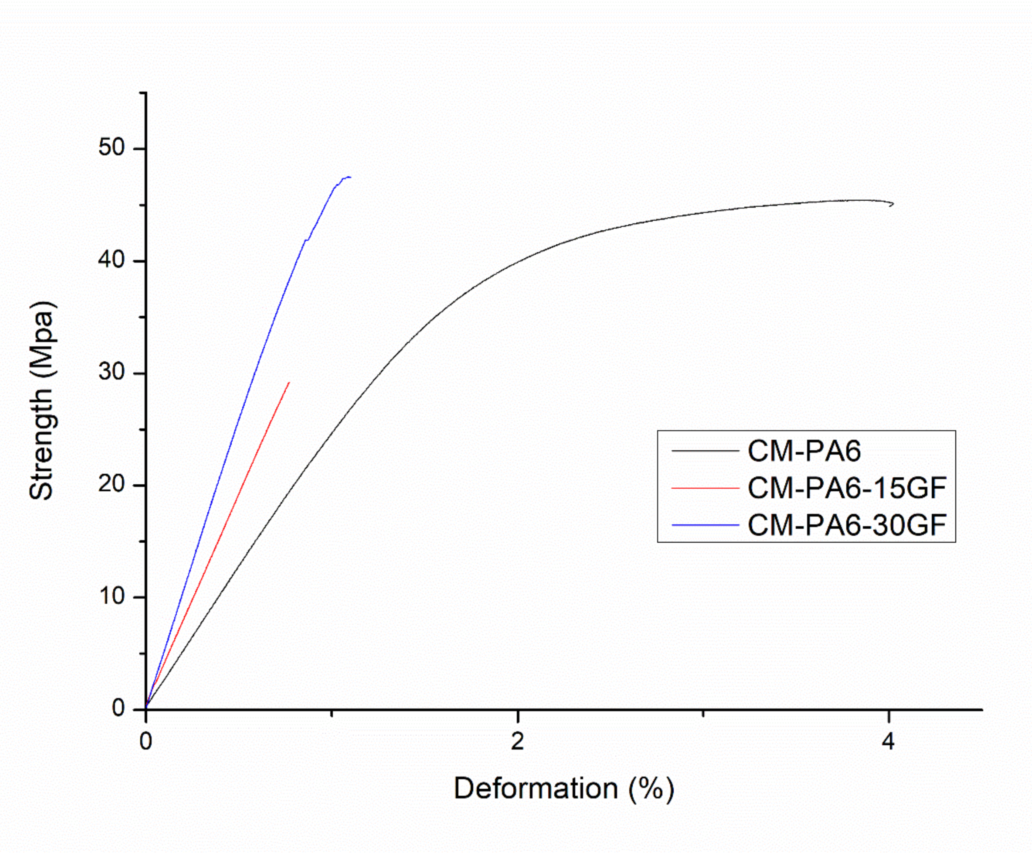


Figure 6.8 Representative tensile curve obtained for compression moulding (CM) samples

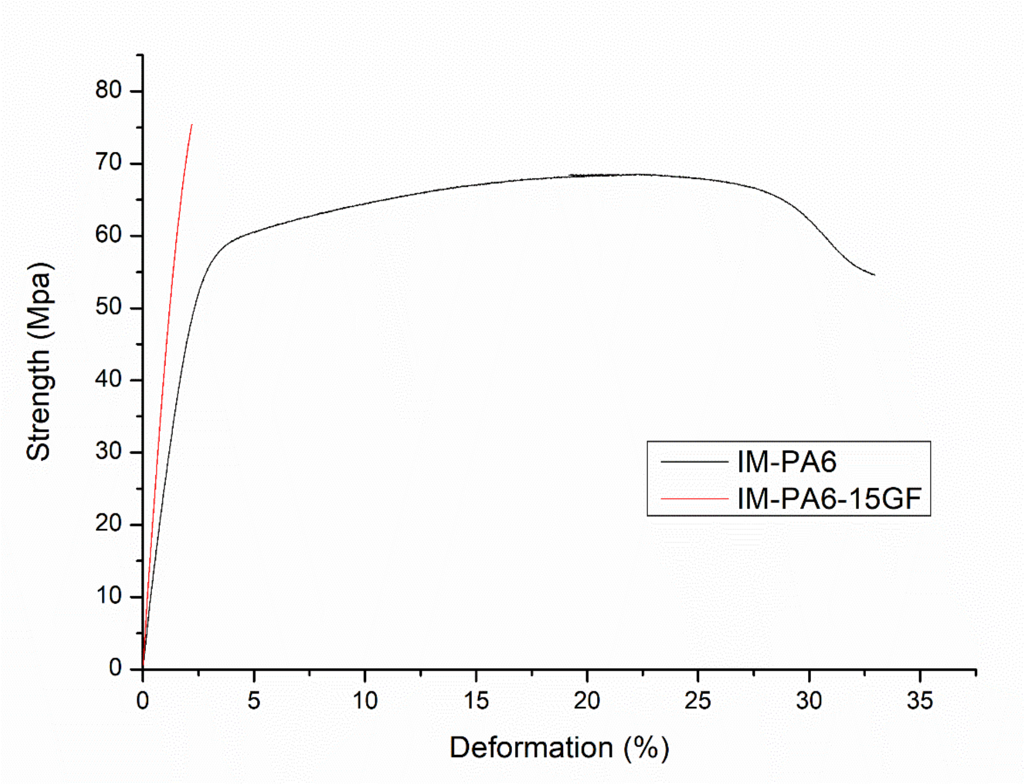


Figure 6.9 Representative tensile curve obtained for injection moulding (CM) samples

6.4 Conclusions

This part of the study was designed to investigate the possibility to operate a mechanical recycling on automotive processing scraps. The recycling process involves grinding, mixing with non-reinforced matrix and compression or injection moulding. The grinding of the laminate leads to the breakage of the fibers which finally show an average length of half a millimetre.

The recycled material can be injection moulded with a 15% of fiber content and compression moulded with both 15% and 30% of fiber content. Compression moulding technologies determines an internal porosity of the product which influences the mechanical properties increasing the dispersion of the tensile strength data.

The recycled polyamide 6 containing 30% of fibers after compression moulding has a higher elastic modulus and tensile strength comparable to a virgin material not reinforced and processed with the same technology. The recycled polyamide 6 reinforced with 15% of glass fibers presents a higher Young modulus but lower tensile strength compared to a virgin non reinforced compression moulded polyamide.

Instead, the injection moulded recycled material with 15% of fibers has both modulus and tensile strength higher than the same non reinforced injection moulded matrix.

In conclusion it can be stated that the mechanical recycling of this type of processing scraps can be used to produce component of commercial interest usually manufactured with unreinforced polyamide 6.

Chapter 7

Final conclusions and remarks

In this thesis work the possibility of using the mechanical recycling method to reuse composite automotive waste was investigated. To this end, two different types of composite automotive waste were recovered: an end-of-life component taken from landfill and production scraps from the thermoforming process of a laminate.

For both products, the mechanical recycling process involves size reduction, pelletizing, and moulding operations to obtain the specimens to be mechanically tested. For the processing scraps a preliminary mixing operation had to be carried out to reduce the percentage of glass fibers. The operations just described confirm that mechanical recycling is one of the simplest and economic methods for recycling thermoplastic matrix composites.

In the case of the end-of-life component, consisting of polyamide 6,6 reinforced with 35% glass fibers, the degradation of the material due to mechanical recycling and its use in operation leads to a worsening of the mechanical properties compared to the same non-aged material. Despite the mechanical recycling operations, the properties in terms of modulus and tensile strength always remain higher than those of a virgin polyamide 6,6 not reinforced.

In the case of recycling of production scraps, made of polyamide 6 reinforced with glass fibers, being the starting material not designed for injection moulding, it was more difficult to use this transformation technique to obtain a high-fiberglass recycled product. Despite this, it was possible to injection-mould the polyamide 6 reinforced with 15% glass fiber after mixing with virgin matrix not reinforced. This product has better mechanical properties than an injection-moulded non-reinforced polyamide 6. Having used a laboratory injection moulding machine, it cannot be excluded that with industrial machinery it would be possible also to mould a 30% glass fiber product. Instead, it was possible to mould both recycled materials reinforced with 15% and 30% of fibers by compression, but only the 30% glass fiber product has better mechanical properties than the virgin non-reinforced polyamide 6.

The results obtained suggest the use of these recycled materials for processing commercial products currently made of unreinforced polyamide or reinforced polyamide with percentages up to 15% in glass fiber. In the automotive sector the possible applications regard components such as carbon canisters, connectors, fasteners, headlight bezels and turbo air ducts.

In conclusion it can be claimed that mechanical recycling can be a solution to the problem of the accumulation of composite materials in landfills since the products obtained after recycling shows characteristics useful for different applications. In order to upscale the process in industrial environment, it is necessary to grant the availability of these composite materials, appropriately collected and selected by type. To achieve this goal, under the pressure of European regulations, the creation of a recycling chain for composite materials is essential.

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