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PON RICERCA E INNOVAZIONE

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SAPIENZA
UNIVERSITÀ DI ROMA

PhD in
Industrial and Management Engineering

Study, design & development of compostable and recyclable elastomers with a high degree of innovation, technological content and low environmental impact

PhD Student:
Chiara Lignola

Tutor:
Professor Annamaria Gisario

XXXVII Cycle

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Abstract

PhD research aim is to design and develop a bio-elastomer with high degree of innovation, technological content and low environmental impact. The research is restricted to the industrial field of automotive applications, focusing on thermoplastic elastomers (TPEs) for o-rings manufacturing. The project focuses on conceiving an eco-friendly elastomer, driven by necessity to mitigate TPEs environmental impact related to their conventional fossil-based nature and disposal.

The research project is a collaboration between Sapienza Università degli Studi di Roma, Department of Mechanical and Aerospace Engineering, and Tresearch S.r.l., an innovative start-up acting as an industrial partner.

The first step has been to investigate bio-based, biodegradable and compostable materials for prototype formulation definition. Three blends have been conceived, selecting a PLA matrix as primary biopolymeric phase. The addition of a liquid biodegradable plasticizer (Acetyl Tributyl Citrate-ATBC) and/or of a secondary biopolymeric phase (P3HB4HB-PHACT) was assessed to improve the flexibility and the elongation of PLA, aiming to design a bio-elastomer with complete elastic recovery. On this point, the three formulations have been respectively named as PLA/ATBC, PLA/PHACT, PLA/PHACT/ATBC. Once formulations have been defined, compounding was conducted via co-rotating twin-screw extruders for lab-scale pellet production. The three blends have then been fed to a single-screw cast extruder for sheet forming. Along with extrusion processes, compound and sheet characterization has been performed: thermal (DSC) and rheological tests (MFI, Rheometer) to characterise the experimental compounds as well as tensile tests on the sheets to evaluate materials elastic behaviour. Based on the analysed performances, PLA/ATBC compound has been identified as prototype bio-elastomer.

Finally, a Life Cycle Assessment (LCA) has been carried out to compare environmental impact of the prototype bio-elastomer with a traditional TPE derived from fossil sources (EPDM). Following a *cradle-to-grave* approach, the environmental impact generated from life cycle single phases of both materials has been assessed and a full comparative LCA performed.

1. Introduction

Today industrial segments such as automotive, health care, building and construction as well as packaging and toys feature a deep range of products largely made by plastics and rubbers. Nevertheless, these materials do not degrade at the end of their life cycle, but remain for a long period in the environment, often not even undergoing the recycling process (4).

Nowadays issues related to environmental impacts such as the significant volumes of plastic waste spilled into the oceans have encouraged the transition to compostable and bio-derived plastics resulting in a strong growth of the bio sector itself. Indeed, bioplastics offer a feasible alternative to traditional fossil source plastics. In this perspective, the design and development of innovative compounds which show end-life biodegradability can contribute significantly to limiting the impact of plastic waste on terrestrial and marine ecosystems.

The PhD project focuses on bio-based thermoplastic elastomers as an alternative to its fossil-based counterpart whose extensive use has led to an increase in the environmental footprint associated with materials processing and end-life disposal. Thermoplastic elastomers, also known as TPEs, can be described as rubbery materials which combine the characteristics of rubber and thermoplastics. TPEs are typically processed through the traditional thermoplastic methods, such as injection moulding, compression moulding, extrusion.

Compared to other materials, elastomer resins show both consistency and elasticity, as well as a low Young's modulus and high yield strain. They are commonly used for different applications, especially in automotive manufacturing, sanitation and biomedical sector.

It is important to point out that TPEs are potentially recyclable, but today recycling is barely pursued due to deterioration of material properties. Because of this decay, most of the time TPEs are incinerated or sent to landfills leading to severe impact on the environment, since they are largely or wholly derived from fossil sources.

The goal of this research is to study and develop new solutions with a high degree of innovation that might mitigate the environmental impact of TPEs, ensuring at the same time the necessary functional properties for final industrial applications.

On this subject a key aspect is that the production of such innovative materials might be done through established technologies, not requiring significant changes to traditional plastic processing plants.

Remarkably this allows to avoid as much capital expenditures (capex) investment as possible in an industry already severely tested by the transition from fossil-derived to materials with a low environmental footprint.

Production of thermoplastic elastomers from fossil sources leads to a significant environmental footprint mainly due to the:

- necessary energy involved for the transformation processes;
- non-renewable raw materials usage;
- high emissions in air and water from the process;
- generation of wastes both during the process and at the end of the life cycle, which is most of the time managed via incineration or landfill disposal.

In summary, the development of innovative thermoplastic elastomers derived by bio-polymers and compostable materials might limit the use of non-renewable sources, the related energy consumption and also the risk associated with the products' end-of-life management. In fact, these materials might be composted or even sent for recycling in full consistency with the policy *a greener, low-carbon transitioning towards a net zero carbon economy* of the React-EU plan.

During the research different studies have been analysed and pursued to gain the expected result: a fully bio-derived, biodegradable and compostable compound, characterised by sufficient flexibility and elastic recovery capacity which is typical of elastomers.

An initial phase of study and design of the formulations has been conducted leading then to an iterative research approach according to the logic of continuous material-process-product optimization.

Polylactic acid blends have been tested and developed by adding functionalized plasticizers and other polymeric phases via reactive extrusion to produce pellets on laboratory scale with the collaboration of the partner company Tresearch S.r.l.

To analyse the specific characteristics of the granules, a laboratory characterization has been conducted on the prototype compounds. Finally, a cast extrusion has been performed in order to obtain sheets for the tensile characterization.

For future developments, final formulations might be subjected to functional assessment to study and check their applicability in the sealing systems gaskets market according to industrial targets.

Thesis structure

This PhD thesis is organized into nine chapters, where Chapter 1 is the introduction. After a description of plastic pollution issue, the introduction deals with Circular Economy principles and illustrates the bioplastic field.

Chapter 2 presents conventional thermoplastic elastomers (TPEs) analysing their features, market and applications with focus on o-rings.

Chapter 3 discusses and investigates bio-based, biodegradable and compostable biopolymers as well as additives for the prototype formulations definition. The aim is to develop an eco-friendly elastomer based on a PLA matrix.

Chapter 4 illustrates prototype formulations compounding via two lab-scale twin screw extruders to produce the experimental compounds in pellet form. While Chapter 5 details compound laboratory characterization via thermal (DSC) and rheological tests (MFI, Rheometer).

Chapter 6 describes the second stage of the extrusion processes: lab-scale single screw cast extrusion to produce prototype sheets. Therefore, Chapter 7 illustrates standard tensile tests performed on the sheets to assess the elastic behaviour of the formulations.

Chapter 8 focuses on Life Cycle Assessment (LCA) analysis, performed with SimaPro software, to evaluate the environmental impact of the most promising prototype bio-elastomer in comparison with a traditional TPE for o-ring production, along with sensitivity analysis on disposal scenario.

Finally, Chapter 9 draws conclusions from the PhD thesis and outlines possible future research studies that might be pursued and implemented to continue the design and development of biodegradable and recyclable TPEs.

1.1 Circular Economy

Every year, on a global basis, production of plastic from fossil sources achieves significant volumes, with a correlated high amount of waste and a raising concern related to its disposal. Therefore, environmental pollution related to plastic has definitely become a worldwide issue due to its resulting impact on ecosystems.

According to the Organization for Economic Cooperation and Development (OECD) reports, annual plastic production is expected to reach 1,2 billion tonnes by 2060. Environmental pollution's main player is disposal with most common solutions being incineration, landfills and the direct dump into the oceans. It is estimated that 25 million tonnes of plastic waste contaminated water will pollute rivers and oceans, with consequent issues for marine ecosystems and human health. Plastics are in fact subjected to degradation into microplastics due to wind, waves and sunlight combined actions (6), facilitating spread and absorption by the ecosystem.

Additionally, the incineration of plastic products made out of polyvinyl chloride (e. g. plumbing pipes used for agriculture and household purposes) might liberate harmful halogenated compounds due to thermal degradation. In wide terms, plastic waste combustion potentially develops the risk of pulmonary and cardiac diseases, endocrine disruption, and many other hazardous damages to human health (7).

According to Zheng J. et al. (14), global life cycle GHG emissions in 2015 from conventional plastics were 1,7 Gt of CO2-equivalent (CO2e) and are expected to raise up to 6,5 Gt CO2e by 2050.

As described by Gnatowski P. et al. (13), although forecast reveal GHG emissions will continue to grow, it is worth taking new initiatives to reduce polymer industry impact on the environment, based on evidence showing there is a correlation between the selection of biomaterials and greener solutions with climate change and sustainability.

In addition, according to Karan Hakan et al. (12) global plastic production up to 2015 exceeded 8,3 Gt and resulted in 6,3 Gt of plastic waste. Only 21% of 6,3 Gt waste has been recycled or incinerated.

While the remaining 79% either was sent to landfill or was released directly into the environment. By 2050, forecasts expect plastic waste to increase toward 12 Gt and recycling figures above would not be sustainable.

Clear evidence of plastic pollution on a global scale is the Great Pacific Garbage Patch: a vast accumulation of debris, primarily plastics, formed due to complex oceanic currents and covering an area of around 1,6 million km^2, steadily expanding. Thus, the rising demand for plastics traditionally derived from fossil sources which fully degrade in many years has highlighted the need to replace more conventional non-degradable plastic with eco-friendly solutions.
Furthermore, to confirm the above mentioned, Burelo M. et al. show that, according to Plastics Europe AISBL data, the global plastics production in 2021 was about 390,7 Mt, while it reached 400,3 Mt in 2022 with estimated production split among countries in these percentages: Africa 9%, Europe 14%, America 21% and Asia 56%, where China alone has reached the highest plastic production of about 32% (18).

On the other hand, the plastic waste issue has encouraged innovation and deep research activities in the bioplastics field, paving the way to alternatives for conventional plastics and suggesting that bio-based plastics might be considered part of an expanding circular bioeconomy (12).

In this regard, the European Union (EU) periodically releases and amends environmental policies and legislation to pursue environmental protection. The European Green Deal has been implemented to gain climate neutrality by 2050, leading to the release of advanced directives and strategies. Hence, European countries have committed to remodel a linear economy into a circular economy characterised by modernity, resource efficiency and competitiveness. On this point, bioplastics might represent significant promoters of the circular economy, providing an eco-friendly contribution (6).

The set of strategies defined and minted since the 2010s are known as “R-strategies” because the key focus is on reducing, reusing and recycling resources.

Geissdoerfer et al. define the circular economy as “a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops. These terms can be achieved through long-lasting design, maintenance, repair, reuse, remanufacturing, refurbishing, and recycling”.

In other words, according to Burelo M. et al. circular economy principles promote efficiency and aim to decouple economic growth from resource depletion and waste generation (18).

1.2 Bioplastics

Global bioplastics production has recently witnessed significant growth and expansion. It is estimated at over 2 million tonnes for 2024 and rises steadily due to the increasing demand as well as the need for more customized products. For instance, European Bioplastics forecasts announce that global bioplastic production will rise from around 2,47 million tonnes in 2024 to almost 5,73 million tonnes in 2029 (8). As of today, comparing the bioplastic market to the annual plastic production of 414 million tonnes registered in 2023, bioplastics' share is <0,5%. However, thanks to the strong development and implementation of bio-based and biodegradable polymers, such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA) as well as many other eco-friendly alternative polymers, bioplastic production capacity is expected to rise substantially within the next 5 years, as shown in Figure 1 and Figure 2.

At the same time, bioplastics fields of application are regularly increasing and might be found far more often in the following industries: packaging, automotive, health care, agriculture, consumer electronics, consumer goods, cosmetic. Specifically, the automotive and medical devices sectors are continuously developing new applications based on biopolymers.

Among biopolymers field, a circular economy strategy reconciles two aspects. Firstly, it supports decoupling from fossil raw materials and contributes to carbon neutrality through the use of recycled and bio-based polymers.

Secondly, it ensures that polymers are collected and recycled at the end of their life-time, or are fully biodegradable and compostable (2).

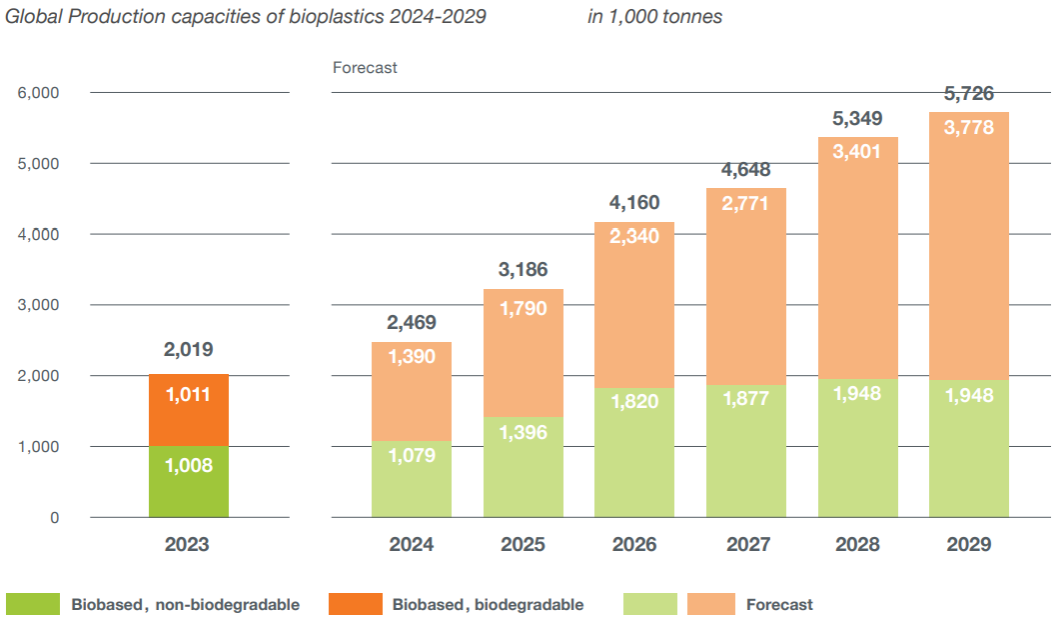


Figure 1 Global production capacities of bioplastics 2024-2029 (8)

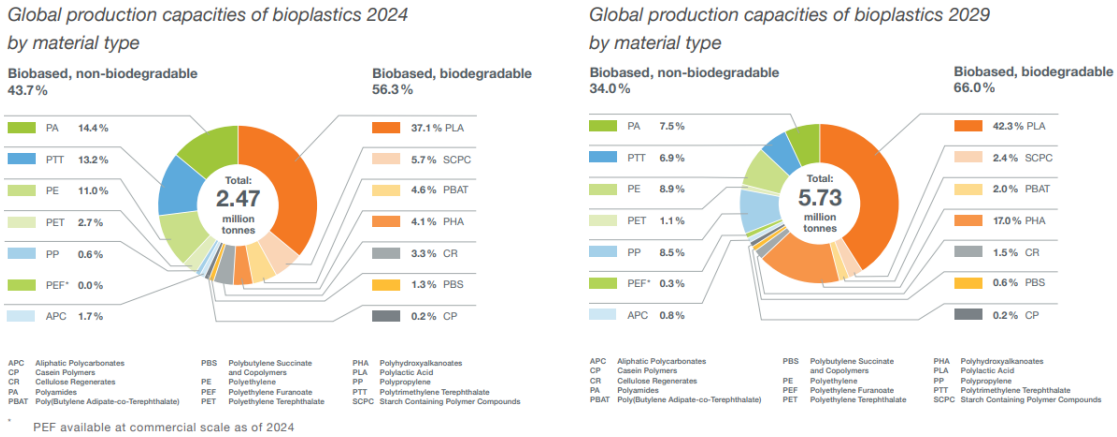


Figure 2 Bioplastics production capacity data for 2024-2029 (8)

In the circular economy approach resources are used for as long as possible, maximizing value extracted during their lifetime, while at the end of the useful life products and materials are recovered.

Within this context, the European Union strategy aims to protect the environment from plastic pollution by limiting the intentional use of microplastics, reducing the consumption of single-use plastics and imposing recycling targets for plastic packaging.

The goal is to achieve a sustainable circular economy: this implies that polymer production must start transitioning from fossil-based to recycled & bio-based feedstock and achieve CO_2 emission neutrality (2).
It is worth noting that the increasing market share of bioplastics might be essential in reducing fossil-based resources exploitation, encouraging the transition to a bio-based society and a circular economy. On this point, a feasible way to increase production volumes of bioplastics is to use waste feedstocks (3).

In relation to bioplastic field, a significant topic addressed in scientific literature is ageing over time. As Latos-Brozio M. and Masek A. describe in their study (68), a wide range of stabilizers has generally been adopted during plastics production to prevent material degradation, due to the action of many elements like UV radiation, temperature, oxygen, etc. The polymers degradation may occur both during the process and the use of the final product. Focus has been recently placed on the use of natural antioxidants to act as stabilizers. Actually, acids with bio-origin belongs to this category, in particular, succinic acid can be used as a functional additive. The study (68) shows that succinic acid might be adopted as an antioxidant for bio polyesters when used at specific concentrations. Depending on the application, by controlling the exact amount of succinic acid, it is possible to extend or shorten the polymer lifetime, slowing or accelerating oxidation resistance respectively.
Literature studies typically show that ageing may affect biopolymers mechanical and thermal properties as well as biodegradation rates. However, the selection of proper additives might extend bioplastics lifetime, depending on the boundary conditions of the application and the ageing factors. Hence, bioplastics durability represents a substantial topic still being studied that requires proper implementation based on the industrial field of the materials object of the study.

2. State of art: TPEs and o-ring applications

Elastomers consist of a class of polymers featuring high elasticity and viscoelasticity, which find several applications aided by their excellent resistance to abrasion, tear and impact. From this perspective, they demonstrate an outstanding capability of restoring their initial form after undergoing stretching or deformation (18).

Elastomers can be classified in two main categories: thermoplastic elastomers or TPEs and thermosets. To the first category belong: thermoplastic polyester elastomers, thermoplastic polyether elastomers, thermoplastic polyurethane elastomers, thermoplastic polyamide elastomers. To the second one: vulcanized natural or industrial rubber, epoxidized natural rubber, cross-linked polyester elastomers, cross-linked polyurethane elastomers.

In recent years, the thermoplastic elastomers market has significantly grown finding application in automotive, bio-medical, aerospace and construction industries, as well as in electronics and consumer goods due to TPEs high technical and functional content, as schematically illustrated in Figure 3 (18).

According to Tang S. et al. (17), TPEs combine elastomers properties with the processability of thermoplastics at high temperature. In fact, TPEs show the most common properties of thermoplastics such as processability and recyclability, with the addition of elasticity and durability, making them similar to vulcanized rubber.

Overall, TPEs represent a valid alternative in the rubber sector thanks to their improved flexibility, durability and design versatility (5). However, elastomers are currently non-recyclable and derive from non-renewable sources (18).

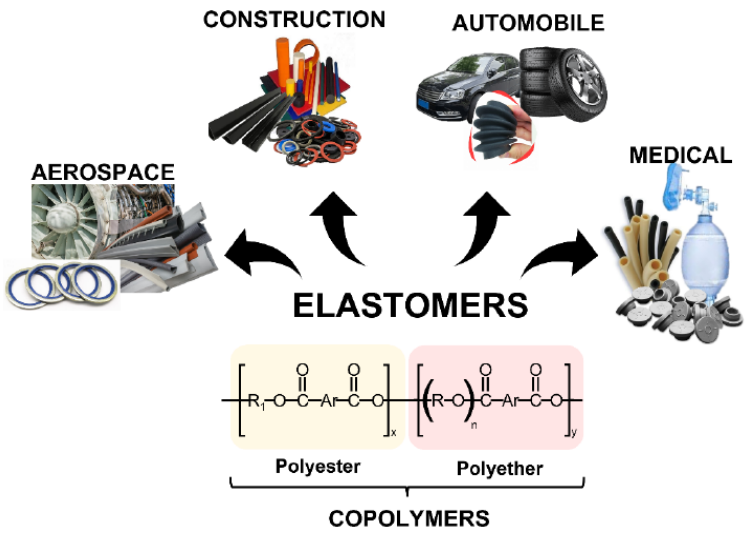


Figure 3 Polyester and polyether elastomers as copolymers: some applications (18)

2.1 TPEs Market trends

TPEs class, which belongs to *specialty chemicals*, has recently reached significant market volumes. Indeed, trends show an annual growth of 3% and forecast further growth at least until 2026.

Thermoplastic elastomers have a potential that might lead to a future industrial transition towards high performance and sustainable materials with a competitive advantage. Certainly, the rubber industry has paid attention to TPEs thanks to their unique blend of thermoplastic and elastic qualities (5).
TPEs industry should be considered a highly strategic market for Europe, thanks to all the positive consequences it might promote, including advanced sustainable products manufacturing with a better performance and streamlined processes (5).

Actually, TPEs are not considered *commodities*, indeed they are *specialty chemicals* with high technical and functional content, so their sale pricing is characterised by mark-ups, if compared to conventional thermoplastic polymers.

2.2 TPEs Classification and properties

Among the rubber industry, TPEs might be considered game-changers. They constitute a family of numerous materials characterised by distinctive qualities and chemical composition that can be used for different industrial applications (5). TPEs class might be synthetized as SBCs, TPUs, TPVs, COPEs, EPR.

Styrenic Block Copolymers (SBCs): Styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) are the two main SBCs. These copolymers are made up of polystyrene, which constitute the hard block, and segments of polybutadiene or polyisoprene, which represent the soft one instead. They show excellent elasticity, flexibility and processability. SBCs can be used for adhesives, soft touch grips, and footwear.

Thermoplastic Polyurethanes (TPUs): thermoplastic polyurethanes are produced via polyols and diisocyanates reaction. TPUs show strength and mechanical qualities, making them suitable for medical devices and automotive applications. TPU formulations allow several material characteristics such as different ranges of hardness levels, from flexible to stiff and impact-resistant.

Thermoplastic Vulcanizates (TPVs): they are characterised by a mixture of cross-linked elastomers, such as EPDM (ethylene propylene diene monomer), and thermoplastic materials, such as polypropylene or polyethylene. TPVs show the advantages of thermoplastic processing combined with vulcanized rubber's performance characteristics: atmospheric agents' resistance, elasticity, and stability at high temperatures. They find application in different sectors such as automotive (e.g. vehicle weather seals), cable insulation, etc.

Copolyester Elastomers (COPEs): copolyester elastomers are made by condensation of diols and dicarboxylic acids. COPEs show excellent flexibility, clarity, chemical resistance and are commonly used in electronics, automobile interiors, and outdoor recreational equipment requiring UV resistance.

Polyolefin Blends: are usually blends of elastomeric materials like ethylene-propylene rubber (EPR) or ethylene-propylene-diene rubber (EPDM) mixed with polyolefin resins like polyethylene or polypropylene. They show flexibility at low temperatures, impact resistance, and weatherability. They are used in industrial applications, home appliances and automotive.

Elasticity and flexibility are among the main TPEs properties worthed to highlight: thermoplastic elastomers can be deformed significantly and, when the stress is released, they return to their original shape. In addition, regardless of elasticity and flexibility properties, they also show good resistance to abrasion and tear. Moreover, depending on the chemical formulation, TPEs may also be resistant to oils, chemicals and greases which make them ideal for the automotive sector. Alternatively, because they can reveal a pleasing sensation when touched, they also find huge application in grips and handles of electronic devices. Last but not the least TPEs are widely processable with established technologies such as extrusion, injection moulding, etc. (5). In Table 1 TPEs classification is represented to compare the different features and industrial applications.

TPE Type	Chemical Composition	Hardness (Shore A)	Tensile Strength (MPa)	Elongation at Break (%)	Specific Applications	Advantages	Disadvantages
SBCs (Styrenic Block Copolymers	Styrene-butadiene or styrene-isoprene block copolymers	40-95	10-30	200-800	Footwear components (soles, midsoles), adhesives, grips	Good elasticity, process ability, cost-effective	Limited weather resistance may exhibit creep over time
TPUs (Thermoplastic Polyurethanes	Polyester or polyether-based urethane segments	60-95	30-80	400-700	Automotive parts (seals, gaskets), medical devices, footwear	Excellent abrasion resistance, toughness, flexibility	Higher cost compared to SBCs, sensitive to hydrolysis
TPVs (Thermoplastic Vulcanizates)	Thermoplastic matrix (e.g., PP, PE) with cross-linked rubber phase (e.g., EPDM)	50-90	15-40	200-600	Automotive weather seals, wire and cable insulation	Good weather ability, chemical resistance, recyclability	Limited high-temperature performance, processing constraints
COPEs (Copolyester Elastomers	Copolyester block copolymers	60-90	20-60	200-800	Outdoor equipment (handles, grips), medical tubing	Excellent chemical resistance, clarity, toughness	Relatively high cost, limited high-temperature resistance

Table 1 Different types of TPEs (5)

2.3 TPEs End-of-life

Materials that belong to TPE class are mainly, if not entirely, fossil-based. The increase in their use has thus led to a rise in the environmental footprint associated with the manufacturing cycle and the end-life disposal.

For instance, if a huge volume of wastes is sent to landfills, circular economy criteria are not respected. Indeed, plastic waste is not yet considered a resource at the end of its life cycle, causing potential environmental damage in the landfill sites themselves (3). As a consequence, the global rise of plastic and rubber waste has led to the necessity of implementing new solutions in order to reuse wastes and reduce the harming effects due to their disposal into the environment (4).
The traditional methods to dispose polymer waste are combustion and landfilling. However, these practices may lead to potential downstream negative consequences such as dust, fumes and toxic gas formation, contributing to air as well as groundwater pollution (4).

Polymer recycling represents the most efficient way to manage plastic wastes both from energetic consumption and environmental impact point of view. Rubber waste might be recycled through size reduction and melt-blended with other thermoplastic resins to produce TPEs. However, TPEs compounds obtained from recycled materials via melt blending exhibit poor mechanical properties. The reason behind this behaviour is that most polymer blends result incompatible and immiscible because of their low affinity and phase separation, e.g. thermoplastic matrix and crosslinked rubber (5).

Nevertheless, the interest for sustainable TPEs such as recycled blends and bio-based TPEs obtained from renewable feedstocks has increased. Therefore, their development might represent a valid more environmental-friendly choice to petroleum-based traditional elastomers, showing a lower carbon footprint and pursuing environmental sustainability (5), thus representing a greener option with a biodegradable and compostable end-of-life.

2.4 O-rings

Because of their good elasticity and chemical resistance, elastomers are one of the primary material groups used for sealing gaskets. The proper selection of the suitable elastomeric seal depends on three main factors: the operating medium; the temperature; the resultant pressure. Last but not the least, another significant factor to be considered is the gradual degradation of the elastomeric seals itself (9). During their life cycle, elastomeric seals develop fatigue cracks and homogeneity variation, leading to mechanical damages in their structure. Indeed, mechanical properties alteration might have a direct impact on safety or on assembly functionalities in which seals are involved. For example, due to their crucial role in the automotive market, automotive industries define the suitability of elastomeric materials through severe qualification requirements (9).
One of the practical applications in the automotive field is sealing gasket for internal combustion engines (ICE), where friction reduction associated with piston travel is necessary to improve fuel economy for a better energy efficiency. In addition, piston rings play a crucial role in regulating fuel consumption, with control rings and seal gaskets preventing leakages through the cylinder wall (10).

Dynamic applications of the o-rings, due to the motion, are more complicated than static applications. There are three types of o-ring dynamic applications (11):

- Reciprocating Seal: a simplified model is illustrated in Figure 3;
- Oscillating Seal;
- Rotating Seal.

Groove dimensions for reciprocating and oscillating applications are the same.

Fluid compatibility must be deeply evaluated because a volume swell of more than 20% may lead to high friction issues, while only a maximum shrinkage of 4% can be tolerated to avoid leakage problems.

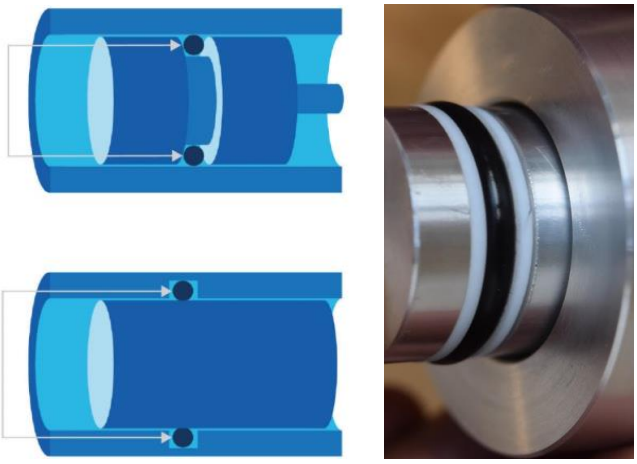


Figure 4 Reciprocating o-ring type -ERIKS (11)

Common elastomeric materials used for seals are: Ethylene Propylene Diene Rubber (EPDR), Polyacrylate Rubber (ACM), Chloroprene Rubber (CR), Fluorocarbon Rubber (FKM), Hydrogenated Acrylonitrile-Butadiene Rubber (HNBR), Acrylonitrile-Butadiene Rubber (Nitrile Rubber) (NBR) and Silicone Rubber (VMQ) (9). Starting from raw rubber materials, a curing process is mandatory to obtain the molecular chains crosslinking and endow elastomer with mechanical properties (9).

Nitrile (NBR) is resistant to oil and chemicals. Due to its properties, it is commonly used in general applications with lubricants and fuels medium. It has an operating temperature range of -20 °C to +100 °C.
Ethylene propylene diene monomer (EPDM) is characterised by resistance to ozone and weathering; it is often used in outdoor applications and water treatment. Among the Fluorocarbon Rubber monomers (FKM), Perfluoroelastomer (FFKM) is known for its excellent chemical and thermal resistance, it is used in chemically aggressive and high temperature environments. Polyurethane (PU) is also used as an elastomer: it is resistant to wear and oils, and it is commonly used in hydraulic systems and high-wear applications.
In order to improve properties such as flexibility, mechanical strength, chemical resistance and thermal resistance, additives are generally used for o-rings production.

Here is a summary of how additives features might affect the o-ring performance:

Curing agents:

Crosslinking of polymer chains is facilitated through the use of curing agents, since they improve strength and elasticity of the o-ring. Common examples include sulphur and peroxide-based agents. Furthermore, crosslinking increases hardness as well as resistance to heat, making o-rings stronger and more reliable.

Plasticizers:

A feasible way to improve o-rings ductility and flexibility is plasticizers addition, optimizing the quantity in the blends. In fact, it is worth to note that an excess in the use of plasticizers may lead to a mechanical strength reduction.

Fillers:

One of the possible solutions to improve both formulations resistance to heat and tensile strength is to add fillers. Concurrently, they can also provide a reduction in the production costs while maintaining performance.

Stabilizers:

O-ring may undergo chemical and thermal degradation: one of the strategies to prevent these phenomena is to conceive formulations with stabilizers, since these additives improve materials protection from UV rays and ozone.

Lubricants:

These additives are not directly added to o-rings during manufacturing, but can be used in dynamic applications to reduce friction between o-ring and contact surfaces. This helps to prevent wear and improve the o-ring life cycle.

In summary, additives are fundamental for tailoring the properties of o-rings to specific applications targets, improving their efficiency and durability.

In Table 2 a description of conventional synthetic rubbers is shown, revealing the main properties and applications, including o-rings and gasket seals.

Rubber	Monomers	Industrial synthesis method	Properties	Applications
Styrene butadiene rubber (SBR)	Styrene Butadiene	Hot emulsion polymerization	More branched, lower molecular weight chain Higher T_g than cold & S-SBR Good dimensional stability Good extrusion characteristics	Lightweight vehicle tire (passenger car, radical car, motorcycle thread), electrical insulation, hoses, seals, haul-off pads, shoe soles
		Cold emulsion polymerization	Better abrasion resistance, tensile strength than hot e-SBR	
		Anionic solution polymerization	High molecular weight linear chain Narrow molecular weight distribution Excellent abrasion and fatigue resistance, mechanical properties Better tire tread traction properties	
Chloroprene (Neoprene)	2-Chlorobutadiene	Emulsion polymerization	High oil and solvent resistance Good thermal, weather, ozone and aging resistance High strength and stiffness resulted from stress-crystallization	Gloves, shock absorber seals, electrical insulation, asphalt, wetsuits, bearing pads
Butyl rubber (IIR)	Isobutylene Isoprene	Cationic slurry polymerization	Excellent water, air and gas permeability resistance Good low temperature flexibility Low compatibility with other polymers, improved by halogenation (CIIR & BIIR)	Stopper, gas masks, sealant, gasket, hoses, o-rings, chewing gum base, waterproof liners
Nitrile rubber (NBR)	Acrylonitrile Butadiene	Hot emulsion polymerization	Excellent oil and solvent resistance High green strength, low flexibility	Engine hoses, seals, gloves, oil and hydraulic seals, o-rings, waterproof fabrics, adhesives, pigment binder
		Cold emulsion polymerization	Less branching chain than hot polymerized Better processability than hot-NBR	
Ethylene propylene diene rubber (EPDM)	Ethylene Propylene Dienes (1,4-hexadiene *etc.*)	Solution polymerization	Wide temperature range of application Good weather, UV, ozone and aging resistance Good resistance to polar fluids, low non-polar solvent resistance Low compatibility with other	Roofings, radiator hoses, door seals, gaskets, electrical connectors & insulators, water tank liners

Table 2 Conventional synthetic rubbers description (15)

The higher demand for synthetic rubber registered in recent decades has led to higher depletion of fossil sources as well as significant environmental effects of overexploitation. Meanwhile, other correlated issues have increased such as the environmental pollution and the expansion of landfills due to rubber and plastic disposal.

In fact, synthetic rubber biodegradation rate is extremely low: after being disposed, rubbers persist in the environment, causing ecosystem pollution and landfill size increase. The rate of biodegradation is extremely low since microbes are unable to digest synthetic rubbers, due to the non-biodegradability. (15)

In summary, an o-ring is a versatile device characterised by a circular form with an annular cross-section. It is generally produced from a wide class of synthetic elastomers and is used for sealing a multitude of both simple and complex applications dealing with liquid and gaseous media. In Figure 5 a typical radial installation of both dynamic and static o-ring is illustrated by Barnwell website.

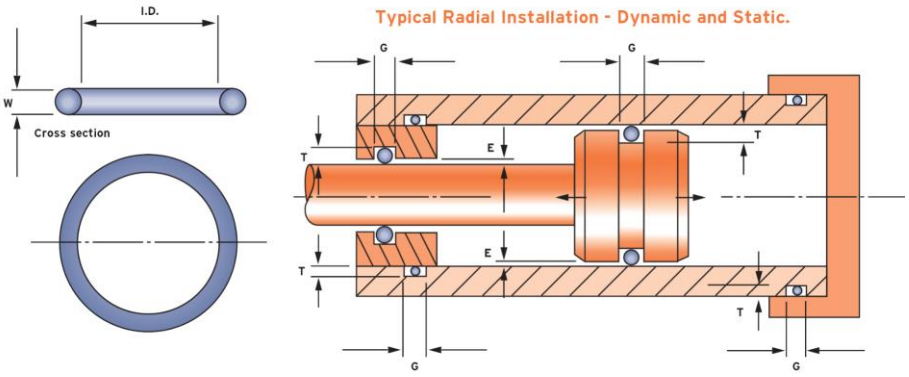


Figure 5 Radial installation of o-ring: dynamic and static (adapted from Barnwell)

Depending on the material, elastomers and o-rings might show different temperature resistance. Here a list of the most common materials used for o-ring application in relation to their temperature resistance:

- NBR: up to 100/120 °C;
- EPDM: -50 °C to 130/150 °C;
- Silicone: -60 °C to 230 °C;
- FKM: ideal for very high temperature resistance.

O-rings are typically used in several machine components to ensure static or dynamic sealing.

Among the wide practical applications, here is a list of the main ones:

- Hydraulic/pneumatic systems: cylinders, valves and pumps (sealing of pressurised fluids).
- Engines: sealing of shafts, pistons and joints (e.g. camshafts, cooling systems).
- Industrial machinery: pipe joints, flanges and heat exchangers.
- Household appliances: coffee machines (sealing of brewing units and solenoid valves).
- Automotive: brake systems, air conditioners and transmissions.

Overall, o-rings are produced via a multi-step industrial manufacturing process, with techniques varying according to size, materials and required standards. Here is a list of the main multi-stages of a typical production process:

1. Mould design: according to the final dimensions of the o-ring, the cavity of the mould is designed. Prior production, the mould is tested for correspondence with the technical drawings.

2. Material selection and preparation: elastomers -natural or synthetic rubber- are mixed with additives such as sulphur, accelerators and fillers to improve heat resistance, elasticity and durability. The choice of material (e.g. NBR, FKM, EPDM) depends on the final application.

3. Forming, which consists of two main manufacturing steps: extrusion and moulding.

- Extrusion process: the elastomer is heated and pressed through a die to create an extrudate, then cut into granules.
- Moulding process: depending on the final application, provides both compression and injection. Material is firstly inserted into the mould and compressed while hot. Then it is forced into the closed mould, ensuring tighter dimensional tolerances. Injection moulding is considered one of the manufacturing processes for large-scale production.

4. Vulcanization: o-rings are not always vulcanized, but vulcanization is the standard and preferred process to ensure high performance and durability. Time and temperature conditions are variable depending on the material.

5. Removal of burrs: residual imperfections called burrs are mainly removed via rotary drum by abrasion; manual polishing; cryogenic deburring.

6. Post-curing and cooling: o-rings undergo additional heat treatment to stabilise mechanical properties and reduce contaminants.

7. Quality control: is an essential step which involves the final check for dimensions as well as absence of surface defects evaluation. Generally, when o-rings are produced by vulcanization, tight dimensional tolerances can be reached.

3. Research and development of formulations

3.1 Bio-based, biodegradable and compostable polymers

The massive growth of plastic waste in landfills and the waste island formation in the oceans has drawn attention to the concept of biodegradable plastics. In fact, according to Lawless S. et al. (27), each year more than 380 million tonnes of plastic are manufactured and this number is expected to double by 2050. With the overuse of plastic and the increasing pressure on its disposal, the need to design products with a low environmental footprint characterized by biodegradation and compostability has become a requirement for industries.

In recent years, following green chemistry principles, great efforts have been pursued to transform the polymeric industry itself, aiming to produce new eco-friendly and low environmental impact materials which show comparable performance to traditional fossil-based, but being bio-based, biodegradable and compostable.

In Figure 6 the value chain and polymers life cycle are shown, distinguished by different colours: green circular loop via the biosphere; light blue technical loops through reuse and recycling; grey "open loop" via carbon capture and utilization (CCU).

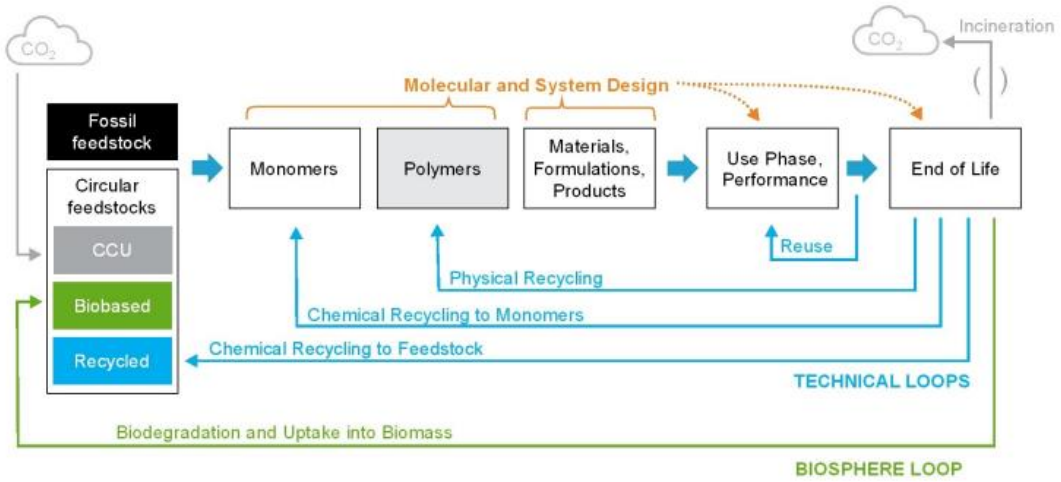


Figure 6 Value chain and life cycle of polymers – Reference (2)

Biodegradation is defined as the mechanism to break down bigger molecules into smaller products by the activity of microorganisms under certain conditions of temperature and humidity. Subsequently the products can be further digested to produce CO_2, H_2O and/or CH_4. Biodegradation process involves the secretion of enzymes by microbes to initiate the breakdown of the material. In this sense, it is essential for the microbes to be able to utilize carbon sources from the material substrate (15). In other words, due to a large number of intracellular and extracellular enzymes, chemical reactions are activated and polymers degrade through a polymeric chain scission. Molecules become smaller and enter a cellular metabolic process, generating energy and transforming into water, carbon dioxide, biomass and other biotic decomposition products. Hence, the biodegradability property does not depend only on the resource from which the material is derived, but is also related to its chemical structure.

As defined by the Italian consortium Biorepack, composting consists in a process of decomposition within a defined time frame and under controlled conditions, which recreate the spontaneous process of turning organic waste into compost, properly closing the waste cycle management. Compost is then used in agriculture, enriching soils with nutrients in a completely natural way (44).

International Union of Pure and Applied Chemistry (IUPAC) defines as “bio-based” materials, those that are either entirely or partially composed of biological products originated from biomass. This encompasses materials derived from plant, animal, marine, or forestry sources (18).

In other words, Burelo M. et al. study (18) illustrates that a “bio-based” polymer derives from natural and/or renewable sources, generally originated from biomass, and reveals a shorter environmental decomposition time, due to both abiotic and biotic factors.

According to Khouri N. et al. (31), biopolymers originate generally from synthesis of renewable natural sources and/or from biological systems such as animals, plants, microorganisms. Alternatively, are produced by chemical synthesis from biological materials e.g. oils, natural fats, starches or sugars.

On the other hand, according to the American Standard for Testing and Methods (ASTM) and the International Standards Organisation (ISO), degradable plastics can undergo significant chemical structure change under specific environmental conditions, leading to loss of physical and mechanical properties that can be measured via standard approaches (31).

3.1.1 Bio-based elastomers

Focusing on the class of elastomers, bio-based elastomers show enhanced properties similar to those of synthetic ones, revealing suitability for a wide range of applications. However, the eco-friendly solutions are characterised by unique chemical functionalities that derive from bio-based building blocks or biopolymers, endowing the resulting elastomers with performance-advantaged characteristics (16).

Furthermore, according to Burelo M. et al. (18) elastomers generally reveal low Young's modulus but high failure strain, despite the viscoelasticity and weak intermolecular forces.

A synthesis of polyesters, polyethers and their copolymers can be made from bio-based sources, such as castor oil, natural rubber, polylactic acid or PLA, lignocellulosic, limonene terpenes, fatty acids, vanillin, tetrahydrocannabinol, among others, providing elastomer properties (18).

A promising class of bio-elastomers is represented by bio-based polyester elastomers, characterised by high biocompatibility and controlled biodegradability. These elastomers can be tailored to achieve different ranges of mechanical properties, from softness to elasticity. In detail, bio-based block copolyester elastomers form a segmented block structure, alternating hard and soft segments. The hard segment provides mechanical reinforcement to the structure, while the soft one gives flexibility. Block copolyesters can be customized by adjusting different properties, such as the structure, ratio and chain length of the soft and hard segments. Among block copolyester elastomers, polylactic acid (PLA) is commonly adopted as the hard segment (16).

In this regard, during the PhD project, a scientific literature study has been conducted on bio-based, biodegradable and compostable polymers, targeting application in the thermoplastic elastomers field (TPEs). To this end, the main properties of commercially available biopolymers and raw materials have been preliminarily assessed, focusing on the development of polylactic acid's blends or PLA.

3.1.2 Polylactic acid

Polylactic acid is an aliphatic polyester mainly derived from carbohydrates fermentation, like corn sugar, sugar cane, potato. According to Khouri N. et al., due to its origin from renewable sources and its biodegradable nature, PLA allows to reduce landfill volumes and amounts of CO_2 when compared to traditional polymers which might degrade in centuries (31).

Thanks to its biodegradable and compostable nature, PLA might contribute to reduce the municipal solid waste (MSW) disposal issue. Furthermore, PLA has a versatile nature: can be processed by a wide range of technologies, such as injection moulding, sheet and film extrusion, blow moulding, foaming, fiber spinning and thermoforming. When compared with traditional polymers, PLA features comparable optical, mechanical, thermal, and barrier properties (20).

The basic monomer of PLA is lactic acid (LA), also called 2-hydroxy propionic acid. This monomer exists as two stereo isomers: L-LA and D-LA as illustrated in Figure 7 showing the different chemical structures (20).

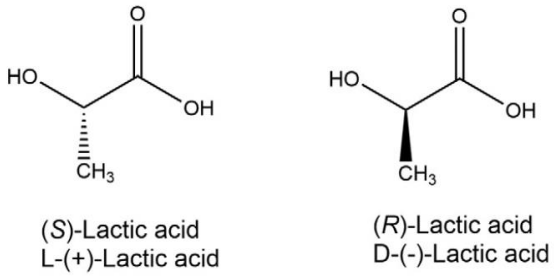


Figure 7 Chemical structure of L (+) and D (–) lactic acid (20)

Depending on the percentage ratio existing between the two stereo isomers L and D, PLA behaves as an amorphous or semi-crystalline polymer.

According to Musienko I. (46), high molecular weight PLA production or Mw PLA is made via several methods, including direct condensation polymerization, direct polycondensation in an azeotropic solution and polymerization through lactide formation, as illustrated in Figure 8. Overall, Mw PLA is particularly recommended for industrial applications.

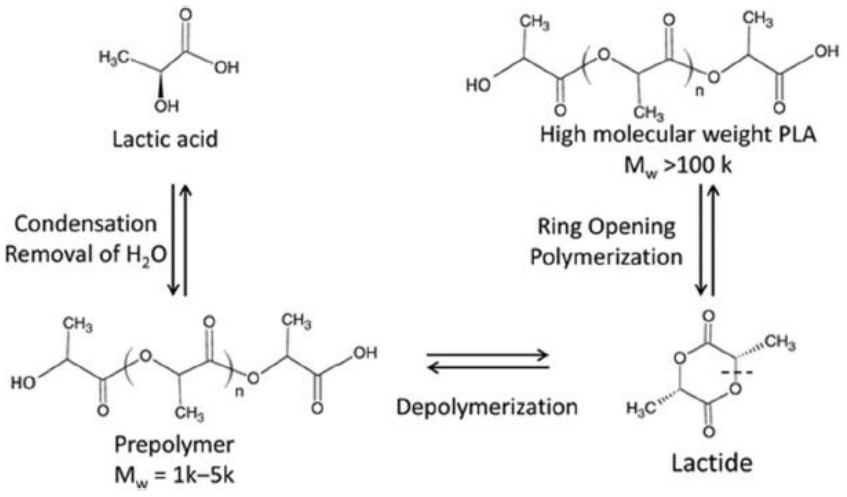


Figure 8 PLA: condensation and polymerization processes (46)

Among the wide class of eco-friendly polymers, PLA might be considered one of the most promising renewable and biodegradable polymers, thanks to its outstanding properties, such as high tensile strength, high modulus, and excellent transparency. However, PLA shows a brittle nature, hence its toughness is typically risen by blending it with other polymers (19).

In this regard, PLA mechanical properties were firstly studied: literature has shown that PLA features high stiffness and strength related to a high value of the elastic modulus.

It is worth pointing out that PLA exists both in amorphous or semi-crystalline state, depending on its molecular distribution, mass, and stereochemistry which thus affect physical, thermal and mechanical properties of the biopolymer (31).

The semi-crystalline structure features ordered regions that increase stiffness and mechanical strength, but limit the mobility of the polymer chains, favouring brittleness.

Amorphous PLA is characterized by a disordered molecular arrangement which allows greater energy absorption under stress, slightly improving toughness.

According to Baiudurah (22), biopolymers properties are mainly improved via adding other polymeric phases, additives, fillers, etc. with the aim to enhance their suitability for the final industrial application.
On this point, additives, plasticizers and polymeric phases have been studied in order to make blends with PLA through scientific literature analysis.

In light of the above-mentioned scientific evidence, PhD research has focused on engineering PLA to develop a full biodegradable and compostable elastomer, improving PLA brittle nature and minimizing the thermo-hydrolytic degradation during the reactive extrusion. In fact, according to Lim L-T. et al. (21) it is well known that, when exposed to elevated temperatures, PLA may undergo thermal degradation, leading to the formation of lactide monomers.

The PhD research, therefore, aimed to find a PLA blend that could match the ductility and strength typical of traditional elastomers with a low environmental impact.

3.1.3 Natural rubber

A wide literature study has been conducted about the addition of natural rubbers (NR) and epoxidized natural rubbers (ENR) within PLA matrix.

Fazli A. and Rodrigue D. (61) define natural rubber as a biopolymer based on cis-1,4-polyisoprene with a bio-origin obtained from *Hevea brasiliensis*. It consists on an unsaturated rubber and exhibits high elasticity and flexibility as main properties.

As reported in Hayeemasae N. et al. study (62), ENR production results from a chemical modification of natural rubber (NR) through epoxidation of NR with formic acid and hydrogen peroxide.

NR and ENR show multiple advantages related to both mechanical properties and environmental sustainability. In fact, they are biocompatible and biodegradable renewable resources characterised by toughness and flexibility, as well as low cost. They might represent one of the viable solutions to engineer PLA, improving its toughness. In fact, natural rubbers feature tough, flexible and impact-resistant behaviour whether functionalized or not. For this purpose, commercially available types of NR and ENR natural rubbers have been studied to assess their suitability for the scope.

From literature analysis (63) it was found that both the quantity and particle size of NR have an influence on the toughness of PLA. Especially the addition of very small particles of NR, in a precise optimized percentage, might lead to an increase in the elongation at break of the biopolymer. Whereas, the addition of ENR within a PLA matrix might reduce its mechanical properties in certain cases.

Furthermore, Pongtanayuta K. et al. (63) found that the ability of PLA to crystallize increases when NR and ENR are blended, while thermal stability is reduced. Regarding thermal properties, PLA/ENR blends show higher thermal stability than PLA/NR blends: in this case, in fact, the cleavage of PLA polymer chains may occur resulting in a decrease of molecular weight and thermal stability.

As described in literature (61), in most cases NR is subject to vulcanization process by sulphur-based curing systems; similarly, ENR is typically vulcanized as well (62).

Since studies have shown that natural rubber, as well as synthetic rubber, is in most cases vulcanized to improve its thermal and mechanical properties, PhD research has focused on the study of plasticizers addition as well as polymeric phases that do not require in the first instance the vulcanization process, making laboratory tests more feasible.

In this regard, a wide range of plasticizers, biopolymers as well as commercial grades of PLA have been investigated in order to evaluate the proper blend that could match thermo-mechanical properties with good processability for the final application.

At the end of the literature analysis, PLA formulations have been conceived and engineered without altering the essential prerogative of the material: the end-life biodegradability and compostability.

Different PLA blends have been engineered through the introduction of a biodegradable plasticizer, the addition of a secondary polymeric phase and finally a combination of the two aiming to endow the matrix with flexibility and ductility.

Among the wide range of biopolymers and plasticizers, Acetyl Tributyl Citrate (ATBC) and P3HB4HB (which will henceforth be called PHACT) have been selected for the research, respectively as plasticizer and secondary polymeric phase. Their selection has been the outcome of a massive study of literature and a set of laboratory tests via twin screw extrusion.

3.1.4 Plasticizers: ATBC

The recent interest for bio-based polymers is considerably growing among industry due to the increasing consciousness of environmental concerns. Active research on biodegradable and compostable polymers has led also to new studies on bio-based plasticizers with the aim to replace synthetic conventional ones, especially in the biodegradable thermoplastics-based packaging applications. Bio-based plasticizers have drawn much more attention as additives in the processing of compostable polymers to significantly boost their properties among industrial applications. Generally, bio-based plasticizers originate from renewable feedstocks synthesis. An evolution of bio-based plasticizers has recently taken place: they can be produced from citrate, epoxidized soybean oil, castor oil, cardanol, isosorbide and many others (1). To mention a few bioplasticizers that can be used in compostable polymers:

- Citric acid plasticizers (CAPs): they are well known for their nontoxic and safe nature that allows their usage in food packaging, medical equipment, and children's toys.

- Epoxidized Soybean Oil (ESO): it is produced via synthesis starting from soybean oil via epoxidation process in the presence of hydrogen peroxide and formic acid.

- Castor oil: a bio-based material which contains about 90% of triglycerides including the fatty acid.

- Cardanol (m-pentadecenyl phenol): it is synthesized by distilling Cashew Nutshell Liquid (CNSL); it might be designed as a promising alternative to phthalate plasticizers, aided by its natural phenolic nature (1).

As described also by Trebuňova M. et al., an increasing industrial trend has been observed aiming to replace traditional plasticizers with natural ones (32). Their concentration and compatibility with the biopolymer matrix result in different properties for the final material, so these peculiarities must be properly evaluated.

In fact, the addition of plasticizers requires evaluation studies to gain good miscibility between the polymer and the plasticizer (32).

According to Lazaro-Hedz C. et al. (24), plasticizers and polymer matrices show different chemical and physical characteristics making their incorporation challenging.

The critical issue to be avoided is the plasticizers migration from the polymer matrix, which often occurs in case of low-molecular-weight plasticizers. This critical phenomenon leads to the antiplasticizing effect and material hardening losing material main features. To avoid this issue, reactive extrusion can be considered as a solution, by enhancing the interaction between the plasticizer and the polymer chains resulting in a reduced migration. In essence, the challenging aim of research in plasticizing polymers is to prevent plasticizer migration while maintaining desired mechanical properties, such as tensile strength and elongation at break (24).

ATBC

Simultaneous studies have been conducted regarding plasticizers, targeting suitability for the bio-based and compostable TPE manufacturing. In this regard, esters and citrate esters, vegetable oils, soybean oil and epoxidized soybean oil were evaluated and investigated.

Following the studies, research activities have focused on the use of ATBC (Acetyl Tributyl Citrate), a bio-based and biodegradable low-molecular-weight plasticizer which belongs to citric acid plasticizers or CAPs. ATBC is derived from citric acid esters and is available in liquid form.

Alhanish A. et Ghalia M. (1) report that the acid citric production reached 2,3 million tons in 2016. Over 50 types of CAPs have been produced at industrial scale, one of them is ATBC that has been largely implemented and industrialized due to its excellent properties, such as good thermal stability, light and water resistance. Tributyl Citrate (TBC) production (Figure 9) as well as Triethyl Citrate (TEC) production takes place via esterification of citric acid, often followed by butyrylation or acetylation of the tertiary hydroxyl group to produce respectively Acetyl Tributyl Citrate (ATBC), Butyryl Trihexyl Citrate (BTHC) and Acetyl Triethyl Citrate (ATEC).

Regarding ATBC, its production generally occurs from TBC via two methods: direct esterification with acetic acid and acetylation in the presence of acetic anhydride. (1)

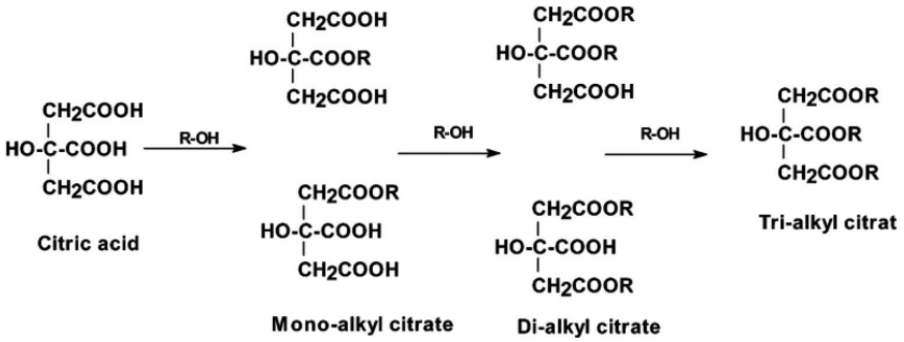


Figure 9 Synthesis of Tributyl Citrate TBC (1)

The addition of liquid plasticizers in bioplastics compounding commonly makes the polymer chains to distance, allowing a reduction in physical interactions; consequently, the compound exbibits a reduction in glass transition temperature (Tg), as will be described in the following chapters. At macroscopic level, this phenomenon leads to a greater flexibility and ductility of the material at room temperature.

Furthermore, plasticizers addition in bioplastics act by increasing the free volume within the polymer matrix, because of their high steric bulk. Again, the effect is reduction of the physical interactions between the polymer chains, with a resulting glass transition temperature decrease and an increase in flexibility. In this regard, literature papers show that the addition of ATBC within a PLA matrix results in an increase in elongation at break and a decrease in tensile strength, as well as a decrease in glass transition temperature (Tg).

In addition, studies reveal that glass transition temperature (Tg) and melting temperature (Tm) of PLA decrease as the amount of ATBC used progressively in the mixture increases. Overall, the incorporation of plasticizers results in lowering transition temperature and improving flexibility and processability (32).

3.1.5 Polyhydroxyalkanoates: P3HB4HB

Poly(3-hydroxybutyrate) or PHB is a biodegradable polyester synthesized from a wide variety of microorganisms. PHB has drawn industrial attention due to its low environmental impact and finds application among agricultural, marine, and medical industries. However, PHB features high brittleness due to its high crystallinity, resulting in a restriction for its application. Moreover, it shows a very narrow window of processability owing to its melting temperature (Tm) which is close to its thermal decomposition temperature. A possible way to lower the crystallinity and melting temperature of PHB is the copolymerization of (3HB) units with other (3HA) or 3-hydroxyalkanoate units. Among the feasible solutions, there is the copolymerization by microbial fermentation of 3HB units with 4HB (4-hydroxybutyrate) units which gives the P3HB4HB polymer. In this regard, over 90 different types of PHAs made up of different monomers have been developed (34). In this contest, trade forecasts show that the global polyhydroxyalkanoate (PHA) market is estimated to increase and to reach 121 million USD by 2025, growing at a CAGR of 14,2% between 2020 and 2025.

In essence, polyhydroxyalkanoates or PHAs can be specifically defined as elastomeric or thermoplastic polyesters of (R)-3-hydroxyalkanoic acids monomers which are obtained by biological synthesis of different gram-positive and gram-negative bacteria as intracellular energy and carbon storage compounds. The pendant alkyl (–R) group can range from methyl group to tridecyl group as there are many hydroxyalkanoate units which are isolated with different -R groups (7).

According to Luo R. et al. description (34), P3HB4HB is produced by *Ralstonia eutropha*, *Alcaligenes latus*, and *Comamonas acidovoran* and shows different physical properties and morphologies depending on the molar fraction of 4HB and their melting points associated with 4HB content. The nature of P3HB4HB manifests in a wide range of forms: from highly crystalline to elastic rubber.

In summary, P3HB4HB is made up of monomers of 3HB and 4HB joined by an ester bond. This polymer is characterised by different structure and a wide range of properties depending on the percentage of 4HB monomer.

It has been observed from literature analysis that, when 4HB monomer is completely absent, the material features heat resistance, brittleness and shows a crystalline nature. On the other hand, when the percentage of 4HB is contained instead between 5 and 15%, the material features a semi-crystalline nature, with fair mechanical properties and moderate heat resistance. As the percentage of 4HB increases, above 30%, the material gets amorphous.

The structure and chemical formula of P3HB4HB is shown in Figure 10. In this thesis PHACT will be used as the abbreviated name of the formula P3HB4HB.
For the PhD research the grade of PHACT selected for the prototype activity is amorphous, features flexibility as well as toughness.

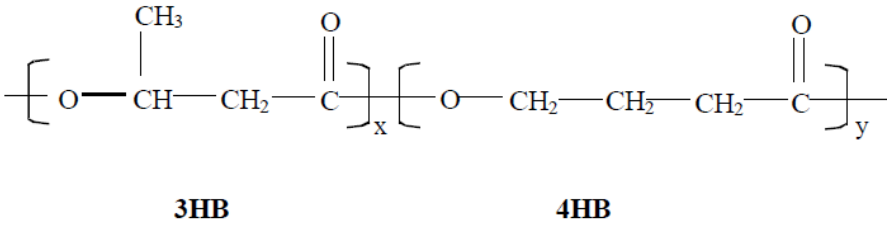


Figure 10 Structure and chemical formula of P3HB4HB (37)

During the PhD research a blend of PLA/PHACT has been investigated to study the performance of P3HB4HB within a PLA matrix. According to Wang X. et al. (35), blending PLA with PHAs represents an effective method for changing and improving the blends properties. As previously described, the ranging molar ratio of 3HB to 4HB can be adjusted providing either highly crystalline materials or soft elastomers. Therefore, P3HB4HB can effectively improve PLA toughness. On the other hand, neat poly(4-hydroxybutyrate) homopolyester features an elongation at break of about 1.000%. Thus, the addition of P3HB4HB significantly improves the elongation at break of PLA films (35).

3.2 Prototype blends

According to Mastalygina EE. and Aleksanyan KV. (57), different solutions can be approached to provide ductility to PLA: (i) copolymerization with more flexible polymers; (ii) compounding with flexible polymers, generally polyesters; (iii) addition of low molecular weight plasticizers or oligomeric plasticizers; (iv) PLA chains rearrangement (57).

Blending is a well-developed technology with lower cost for improving polymer properties if compared with copolymerization. (34) In this regards, three blends have been developed and engineered, which can be identified within two classes depending on the type of PLA adopted: (i) semi-crystalline PLA; (ii) amorphous PLA. The first type might be evaluated as a lower limit case of study since it analyses a standard PLA; the second typology might be considered as a more challenging upper limit case, based on a special grade of amorphous PLA which features high transparency together with grease barrier.

The so-called formulation PLA/PHACT belongs to the first class and it is characterized by the addition of PHACT to a matrix of a semi-crystalline PLA. The so-called formulations PLA/ATBC and PLA/PHACT/ATBC belong to the second class: they share the addition of a low molecular weight plasticizer (ATBC) to a matrix of amorphous PLA, but are distinguished by the introduction or not of PHACT within the blend, as shown in Table 3.

Blend	Matrix	Secondary Polymeric phase	Plasticizer
PLA/PHACT	PLA	PHACT	-
PLA/ATBC	PLA	-	ATBC
PLA/PHACT/ATBC	PLA	PHACT	ATBC

Table 3 Prototype blends formulation

Since the PhD project has been conducted in collaboration with the industrial partner Tresearch S.r.l., the trade names of the materials used and the blending percentages adopted are not disclosed for confidentiality reasons.

Nevertheless, weight percentages of the blends constituents, especially the amount of plasticizer to add, are the result of literature studies and laboratory tests.

Generally, both the semi-crystalline and the amorphous grade of PLA can be processed either with cast extrusion or injection moulding: the grade to be used depends from the process itself and the final application.

For instance, during the PhD project the research has been conducted on a laboratory scale cast extruder which has allowed to produce first prototype sheets.

Relative specimens were then assessed with tensile standard tests to evaluate mechanical properties of the prototype blends.

In case of injection moulding for industrial production of o-rings, the blends might be further engineered both through the addition of specific additives and the use of the suitable PLA grade. However, in the frame of PhD, this process would have required the construction of an expensive ad hoc designed mold.

The PhD research activities have been conducted in collaboration with Tresearch S.r.l. together with laboratories shared between Sapienza Università degli Studi di Roma and Università degli Studi Roma Tre.

4. Reactive extrusion

PLA is mainly processed via polymer manufacturing techniques applied for traditional polymers like Polystyrene (PS) and Polyethylene Terephthalate (PET). One of the leading techniques for mass production of PLA with high average molecular weight (Mw) is melt processing. In fact, the extrusion process aims to achieve an excellent melt viscosity for further manufacturing processes. However, PLA has processing limits, like thermal degradation and poor homogeneity. On this point, during PLA extrusion the temperature profile should always be controlled to prevent thermal degradation. This phenomenon can be attributed to several factors, among which hydrolysis in presence of water contamination (thermo-hydrolytic degradation). Because of this, PLA is generally dried during industrial production (20). Furthermore, thermal degradation can be attributed both to the processing temperature profile and to the stationing time in the extruder and hot runner (21). Other possible causes to mention are: (i) zipper-like depolymerization, (ii) oxidative, random main-chain scission, (iii) intermolecular transesterification to monomer and oligomeric esters, (iv) intramolecular transesterification resulting in monomer and oligomer lactides of low Mw formation (20).

In light of the above-mentioned considerations, analysing thermal and rheological properties as well as understanding crystalline or amorphous nature of PLA might contribute to find and optimize the processing window (20). Furthermore, the extrusion of commercial PLA resins should be processed via extruders regularly adopted for polyesters or PS. The extruder makes the polymer resins molten, providing heat via heater bands wrapped around the barrel. Nevertheless, heat is also supplied by the friction of the resin between the screw and the barrel.

During the PhD research, the main existing technologies for thermoplastic polymers extrusion have been analysed, as well as the specific requirements for biopolymers compounding process such as the extrusion equipment. In this regard, lab-scale extruders have been studied together with the extrusion parameters such as dosages, temperature profiles, screw speed, etc.

Generally, reactive extrusion of plastic polymers can be divided into the following processing steps:

- Feeding of formulation's constituents;
- Heating and melting: the heat is generated both by specific heating systems and friction phenomenon;
- Mixing and conveying;
- Compounding and pellets production.

Furthermore, extruders are usually equipped with boundary sub-systems:

- A feeding system for plastic granules / additives;
- A heated barrel with the relative screw system;
- A die which is designed with specific holes to achieve the desired profiling of the extrudate.

Regardless of the specific process, extruders allow the screw to rotate at a defined processing speed compensating the counter torque generated by plastic granules, as described by Patil H. et al. (39). The twin screw extruder (TSE) features a wide range of advantages over the single screw extruder (SSE). In detail, TSE is widely employed among several industrial applications, allowing a better material dispersion, a lower tendency to overheat as well as a flexible configuration which facilitate the optimization of the process, controlling the set-up parameters. By way of example, in Figure 11 three different screw profiles with related L/D ratio - screw length to outer diameter - are illustrated from Patil H. et al. (39) studies:

- Thermo Fisher standard configuration, 40:1 L/D;
- all conveying elements, 40:1 L/D;
- from left to right, 110 mm of conveying elements, 22 mm of perpendicularly arranged mixing elements and 165 mm of conveying elements 25:1 L/D.

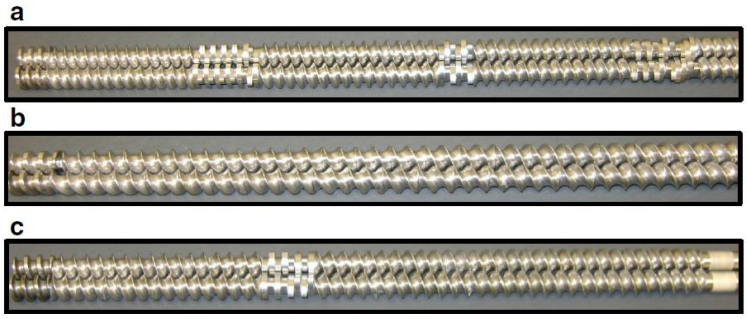


Figure 11 Examples of twin screw configurations (39)

Among the different screw extruder typologies (single, twin, Farrell-Pomini), twin screw extruder is strongly recommended for polymer blends reactive extrusion and particularly for biopolymers. Twin screw extruders can be classified according to the direction of the screw's rotation into: co-rotating extruders, when the screws rotate in the same direction; counter-rotating extruders, when the screws rotation occurs in the opposite direction (42). In this regard, relevant scientific literature studies show that the co-rotational motion of the screws opposed to the counter-rotation typology allows lower mechanical stresses on the material and improved dispersion of the additives and fillers, resulting in a better distribution of the blend constituents. On this point, the twin screw is characterized by proper feed and mixing profiles.

Several parameters might influence the success of a reactive extrusion, here is a list of the main ones:

- Geometry of the screw with its designed length and diameter, as well as pitch and mixing elements. In this sense, the screw provides melting and conveying function as well as increases the pressure into the barrel.
- Temperature along the barrel: the gradient generated in the different sections can be manually controlled via heating and cooling systems;
- Pressure at the end of the barrel: it depends on the components located downstream and is affected by both the flow rate and the speed; pressure may influence the extrudate cut in pellets.

According to the weight proportions established by a blend recipe, the different constituents have to be fed, such as granules, additives in powder or liquid form, fillers, etc.

Therefore, dosing systems are required to feed the materials according to their form. For the addition of liquid additives, a dosing pump is required; while regarding granules feeding, a volumetric dosing unit is used. The volumetric feeder enters a specific volume of material as a function of time and can be manually set according to the calibration curves previously calculated. For powder feeding, instead, a gravimetric dosing unit is employed since fluctuations in material density or flow interruption phenomena may occur during the process. The gravimetric unit is equipped with a computer and a load cell to continuously control and adjust the weight of the feeder and its content; in essence, it automatically manages the dosing rate during the extrusion. Furthermore, extruders may be equipped with vent ports on the barrel to allow the volatile elements to be evacuated. These ports may be used at the same time to feed specific additives or fillers. On this point, twin screw extruders (TSE) feature a better performance to evacuate gases from the barrel than single-screw extruders (SSE).

By way of example, some of the main extruders on the market are illustrated in Figure 12 (39) according to their capacity (kg/h), screw diameter (mm) and screw assembly.

Company	Extruder	Capacity (kg/h)	Screw diameter (mm)	Screw assembly
Thermo Scientific	Pharma mini-HME micro-compounder	0.01–0.2	Variable	Co- and counter-rotating
	11-mm parallel twin-screw extruder	0.02–2.5	11	Co-rotating multiple elements
	HAAKE MiniLab II micro-compounder	0.01–0.2	Variable	Conical co- and counter-rotating
	EuroLab 16XL	0.2–10	16	Parallel co-rotating
	HAAKE Rheomex PTW 16 OS	0.2–10	16	Parallel co-rotating
	HAAKE Rheomex PTW 24 OS	0.5–50	24	Parallel co-rotating
	HAAKE Rheomex PTW 100 OS	0.2–5	Variable	Conical counter-rotating
	Pharma 16 HME	0.2–5	16	Parallel co-rotating
	TSE 24 MC	0.2–50	24	Parallel co-rotating
Leistritz	Nano16	0.2–0.8	16	Co-rotating
	ZSE 18 HP PH	0.5–7	18	Co-rotating
	ZSE 27 HP PH	2–60	27	Co-rotating
	ZSE 40 HP PH	20–180	40	Co-rotating
	ZSE 50 HP PH	60–300	50	Co-rotating
Gabler	DE 40	5–100	40	Co-rotating
	DE 100	80–800	100	Co-rotating
	DE 120	80–800	120	Co-rotating
Coperion Brabender	ZSK 18–70 Twin-screw stand-alone	–	18–70	Co-rotating
	TSE 20/40	–	20	Co-rotating

Figure 12 A list of extruders on the market (39)

4.1 Laboratory extruders

4.1.1 Haake 24 mm

PLA/ATBC and PLA/PHACT/ATBC prototype formulations have been compounded using the laboratory scale twin screw extruder Haake Thermo Scientific Rheomex PTW 24MC (Modular compound) with the required boundary equipment; it is shown below in Figure 13. Haake is a modular twin screw co-rotating extruder equipped with a volumetric feeder for pellets introduction upstream the screw and a gravimetric dosing unit to feed powders along the barrel to provide the correct incorporation in the lowest viscosity zone.

Figure 13 Overview of the lab-scale extruder

The overview of the Haake 24 mm extruder involves:

- a gearbox/coupling between the prime engine and co-rotating twin screw;
- the extrusion barrel divided in 10 sections;
- a single screw volumetric dosing unit for granules placed in zone 1;
- filament cooling bath;
- cutter unit and pellets collector.

As above-mentioned, the extruder is equipped with co-rotating twin screw characterised by a diameter of 24 mm and a L/D ratio of 40.

As previously described, the L/D ratio is a parameter which represents the length of the screw to its outer diameter. This category of screws allows optimal control of biomaterial stationing time as well as gradual heating during the process. As shown in Figure 14, the screw profile adopted for the tests is designed for bio-derived materials, specifically for PLA processing.

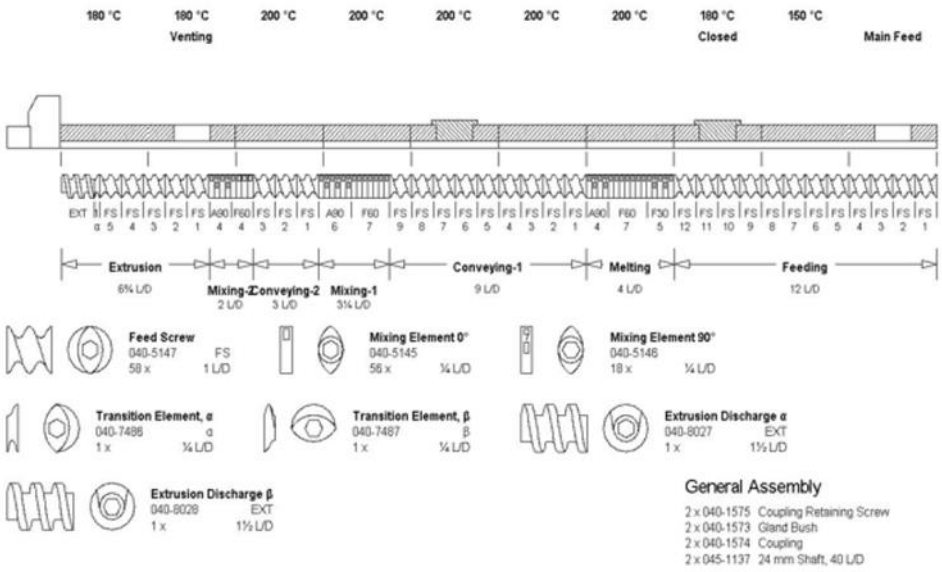


Figure 14 Screw profile - Haake 24 mm

Screw feed profiles allow the material to advance along the barrel, while mixing profiles provide better dispersion of the blend's constituents to achieve a compound with homogeneous characteristics. The twin screw is placed inside the barrel which is divided into 10 independently controlled heated zones which allow to adjust the temperature profile.

Figure 15 Twin screw extruder Haake Thermo Scientific Rheomex PTW 24MC

Observing in the extrusion direction the Haake extruder (Figure 15), from right to left, the 10 sections of the barrel are designed to provide proper features:

- Section 1: granules feed zone;
- Section 3: liquid additives feed zone;
- Section 6: powders and additives feed zone;
- Section 8: vacuum pump, functional for the suction of gases that may generate during the extrusion and have to be eliminated not to compromise the process;
- Section 10: extrusion die from which polymer filaments exit. It is called *spaghetti* die due to its specific shape: there are 3 holes, each one with a diameter of 3 mm.

Downstream of the extrusion barrel are located the cooling system and the cutting unit. The extrudate exiting the *spaghetti* die travels through a water bath where is cooled (Figure 16) and then guided to the cutting system, where pellets are generated and collected.

Cutting unit consists of a circular pelletizer featuring adjustable blades speed to define the pellet size, as shown in Figure 17.

Figure 16 Extrudate exiting the die and passing the cooling bath

Figure 17 Cutting unit and pellet collector

4.1.2 Leistritz 27 mm

The twin-screw extruder adopted for PLA/PHACT extrusion was Leistritz ZSE 27 iMAXX which features an L/D of 40, equal to Haake extruder, but with a twin-screw diameter of 27 mm. This configuration achieves better performance in terms of material transport, mixing and heat exchange. Leistritz is generally equipped with one volumetric feeder to dose pellets, two gravimetric feeders for powders and finally a side-feeder to eventually dose powder additives.

The geometric configuration of the screw has been designed to optimise the mixing of the constituents of the blends. The screws are placed inside the barrel divided into ten zones, equipped with thermocouples for temperature measurement. Each zone can be heated or cooled by manual adjustment on the control panel in order to optimize the processing window, as shown in Figure 18 a.

For PLA/PHACT lab-scale extrusion, Leistritz was equipped with the same cooling bath (Figure 18 b) and pelletizer system of Haake extruder in order to obtain granules with similar shape and size.

Figure 18 a) Leistritz ZSE 27 iMAXX, b) cooling system

It is worth underlining that a 27 mm extruder can be also considered as a pilot scale extruder, since it allows to reach high production volumes. In fact, the optimization of PLA/PHACT extrusion has been a more demanding process, considering the volumes involved compared to Haake reactive extrusions. Generally, in case of extruders pilot scale the value of the torque must be monitored at the initial stage of the extrusion process, since it should not exceed the maximum machine value for the extruder; in this case it is about 70%. Furthermore, it has to be ensured that the value of the polymer melt pressure (P_melt) is achieved to allow a good extrudability of the blends.

4.2 PLA/ATBC first reactive extrusion

In light of the studies described in the previous chapters, the use of ATBC within a PLA matrix has been experimentally evaluated by implementing a laboratory-scale reactive extrusion. For this purpose, biopolymers compounding and processability have been investigated. The lab-scale extruder adopted was Haake 24 mm which has been previously described, equipped with a co-rotating twin screw. This screw guarantees an optimal plasticisation of biopolymers and is characterised by a better performance in terms of mixing and conveying. In essence, the lab-scale plant adopted for PLA/ATBC extrusion is equipped with: (i) a twin screw co-rotating extruder designed to extrude biopolymers; (ii) auxiliaries; (iii) a cutting unit.

Regarding auxiliaries, a volumetric dosing unit was used to feed the resin granules and a peristaltic pump to feed the plasticizer in liquid form (ATBC). As the polymeric material travels through the barrel, it melts through the joint action of heat resistances and friction generated by the twin-screw. Specifically, the extrusion barrel is divided into 10 zones individually thermoregulated that can be controlled and adjusted via a control panel. During the extrusion, it is essential to set both a suitable temperature profile to ensure material processability, and a proper screw speed. On this point, parameters have been regulated to avoid bioplastic material overstressing as well as thermo-hydrolytic degradation.

Meanwhile, temperature profile was adjusted to ensure sufficient stationing time of the material inside the barrel. In this regard, raw material suppliers typically provide guidance regarding the recommended temperature profile as well as the drying conditions. Therefore, the first extrusion attempts were based on the already known info. For PLA/ATBC several attempts have been carried out with a trial-and-error approach to define the optimal temperature profile.
After an iterative optimization of the machine parameters and settings, the optimal processing window was found for PLA/ATBC first extrusion. Table 4 shows a synthesis of both temperature profile and screw speed.

The pellets obtained at the end of the reactive extrusion are illustrated in Figure 19, showing optimal transparency; after the process, tackiness was observed by pellets agglomeration into small blocks.

Figure 19 PLA/ATBC pellets from first laboratory extrusion

Figure 20 Polymeric filament of PLA/ATBC

PLA/ATBC										
Screw speed (rpm)	***Temperature profile (°C):***									
120	***T1***	***T2***	***T3***	***T4***	***T5***	***T6***	***T7***	***T8***	***T9***	***HEAD***
	170	180	180	195	190	185	185	180	170	170

Table 4 Screw speed and temperature profile setting for PLA/ATBC first extrusion

From first qualitative analysis of the transparent filament (Figure 20), PLA/ATBC resulted as an elastomeric material since it was able to fully recover its initial geometry after stress release. In fact, a qualitative tensile test showed that the polymer filament exhibited a high elongation, reaching more than double its initial length (from 20 to 50 cm) and subsequently showing a nearly complete elastic return (22 cm), as illustrated in Figure 21.

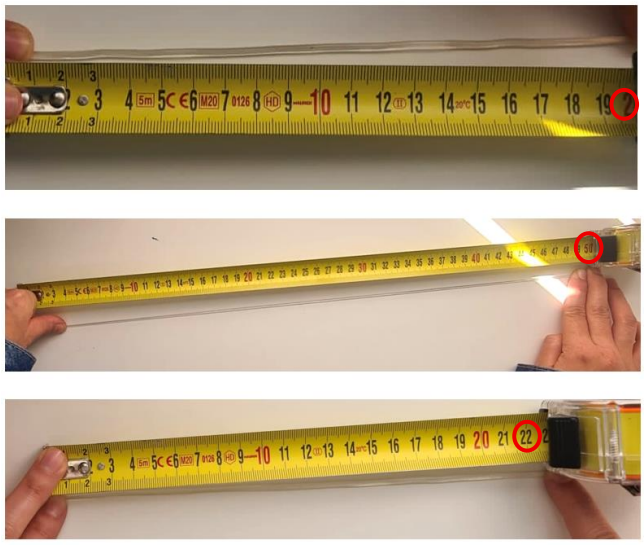


Figure 21 Qualitative tensile test on PLA/ATBC polymeric filament

4.3 PLA/PHACT reactive extrusion

Since PHACT features a high rate of biodegradation and is expected to provide ductility to semi-crystalline PLA, the addition of P3HB4HB (or PHACT) within a semi-crystalline PLA matrix has been investigated and experimentally tested via a reactive extrusion. PLA/PHACT blend has been compounded via a co-rotating twin screw extruder with a screw diameter of 27 mm: Leistritz 27 mm extruder, described in the previous paragraphs. In this regard, Leistritz has been adopted as twin-screw extruder since there was no need to dose a liquid additive during the extrusion which, at the time of the research, could only be dosed on Haake. Before extrusion process, raw materials have been air-dried at 60 °C in an air dryer (Drymax e30 – Wittmann) for 8 hours to minimize thermo-hydrolytic degradation phenomena.

Granules of PLA and PHACT were fed into the extruder according to the weight percentages of the formulation. The extrudate was then cooled in a water bath and pelletized, as illustrated in Figure 22 a and b. The extrudate featured a rubbery-like behaviour and appeared as a stable filament; the pellets were cut and showed a yellow colour due to the PHACT addition.

In the first extrusion attempts, temperature profile has been set according to the melting range of PLA since it constitutes the matrix of the blend and represents the primary polymeric phase. In this regard, the temperature in the first sections of the barrel has been set below the melting value of PLA, since in these zones the screw acts as transporter for the material. In the following mid zones, temperature has been slightly increased above the melting temperature, to facilitate the dispersion of PHACT among the PLA matrix. Finally, temperature has been gradually decreased to rise the polymer melt-strength.

In essence, the temperature profile was iteratively adjusted, starting from the already known melting temperature of PLA. While approaching the mid zones the temperature has been risen and then approaching the extrusion zone has been slightly decreased to facilitate the molten polymer exiting from the die as well as to give higher melt-strength.

Regarding the screw speed, at the beginning of the extrusion it was set at 180 rpm, but then has been increased due to a rise observed in torque signals amplitude. Meanwhile the flow rate has been kept constant to lower the filling rate in the barrel and optimize the process.

The extrusion processing window has been iteratively optimized in terms of processing parameters: volumetric flow rate, screw speed, temperature profile. The optimized processing window is shown in Table 5.

PLA/PHACT										
Screw speed (rpm)	***Temperature profile (°C):***									
350	***T1***	***T2***	***T3***	***T4***	***T5***	***T6***	***T7***	***T8***	***T9***	***HEAD***
	175	185	190	190	185	180	175	175	175	180

Table 5 Screw speed and temperature profile setting for PLA/PHACT extrusion

Figure 22 PLA/PHACT: a) extrudate, b) pellets

The processing window set for the reactive extrusion of the blend PLA/PHACT is illustrated in the panel picture in Figure 23. As shown below, melt temperature briefly called T_melt reached 190 °C, while melt pressure or P_melt was about 50 bars.

Figure 23 PLA/PHACT reactive extrusion parameters

4.4 PLA/ATBC and PLA/PHACT/ATBC reactive extrusion

Considering the outstanding results observed for PLA/ATBC formulation during the first phase of the PhD project together with the promising results obtained from the PLA/PHACT characterization, a new formulation has been implemented: PLA/PHACT/ATBC, combining the addition of PHACT as secondary polymeric phase and ATBC as plasticizer. Hence, the two blends PLA/ATBC and PLA/PHACT/ATBC were compounded, one after another, and then compared.

Reactive extrusion of the two blends was performed via the co-rotating twin-screw extruder Haake, following the optimized processing window set during the first PLA/ATBC reactive extrusion on lab-scale, allowing at this stage an increased screw speed. It is worth to say that screw speed is a significant parameter since the rotational speed may affect the material flow rate and melt temperature, generating higher friction stresses.

The temperature profile and screw speed set for the two blends are shown respectively in Table 6 and Table 7, as well as in Figure 24.

PLA/ATBC										
Screw speed (rpm)	***Temperature profile (°C):***									
500	***T1***	***T2***	***T3***	***T4***	***T5***	***T6***	***T7***	***T8***	***T9***	***HEAD***
	170	180	180	195	190	185	185	180	180	170

Table 6 Screw speed and temperature profile setting for PLA/ATBC extrusion

PLA/PHACT/ATBC										
Screw speed (rpm)	***Temperature profile (°C):***									
400	***T1***	***T2***	***T3***	***T4***	***T5***	***T6***	***T7***	***T8***	***T9***	***HEAD***
	165	175	175	190	185	180	180	175	175	165

Table 7 Screw speed and temperature profile for PLA/PHACT/ATBC extrusion

Figure 24 Extrusion set-up parameters: a) PLA/ATBC, b) PLA/PHACT/ATBC

At the beginning of the extrusion, low speed and flow rate values have been set; then both values have been increased until a reduction in torque was registered. In fact, torque is closely connected with extruder speed and filling rate as well as material viscosity along the barrel. Finally, the extrusion process has been stabilized.

The polymer extrudates exiting the die are illustrated in Figure 25. Both filaments were stable at the end of the extruder and featured high elasticity. The extrudate stability usually depends on the temperature profile set. In fact, in the exit zone of the barrel temperature should be lowered not to compromise the melt-strength of the material.

After the cooling bath, the PLA/PHACT/ATBC filaments were not correctly pelletized in the first extrusion attempts; then, the iterative setting of parameters has led to the optimized processing window.
In this regard, pellets presented almost the same size, related to the cutter set-up that optimized the filament pulling speed with the rotating blades speed.

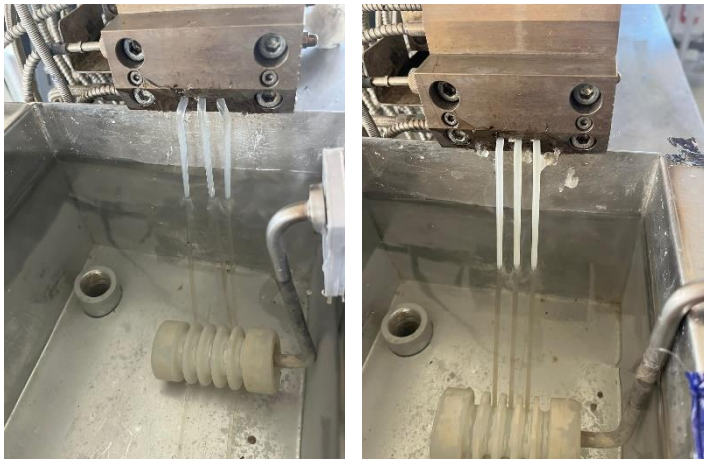


Figure 25 a) PLA/ATBC extrudate, b) PLA/PHACT/ATBC extrudate

Furthermore, both formulations pellets have shown a tackiness nature immediately after the extrusion with a resulting tendency to agglomerate; however, mixing pellets in a planetary mixer facilitated the granules to separate again. As illustrated in Figure 26, PLA/ATBC pellets (a) were perfectly transparent, while PLA/PHACT/ATBC pellets showed a more yellow colour due to the PHACT addition.

Figure 26 a) PLA/ATBC pellets, b) PLA/PHACT/ATBC pellets

At the end of the reactive extrusion, a qualitative tensile test has been performed on both polymer filaments obtained and collected before the cutting unit. From the qualitative test PLA/ATBC blend has achieved more than twice its initial length and has shown complete elastic recovery; PLA/PHACT/ATBC filament has exhibited lower tensile strength, achieving more than three times its initial length and showing a slight residual strain once stress released.

5. Compound laboratory characterization

Laboratory characterization of biopolymeric materials might involve plentiful tests to assess thermal, rheological, chemical and mechanical properties, which are important for quality check and production processes optimization.

During the PhD project, once the extrudability of the formulations has been assessed and the extrusion process of the bioplastic granules implemented, the laboratory characterization of the three compounds has been outlined by a wide class of analyses. Focusing on rheological and thermal analysis evaluation, here is the recap: Melt Flow Index (MFI), Rheometer and DSC analysis.

5.1 Rheological analysis

According to Picout D. and Murphy S. (28), rheology studies the flow and deformation of materials and illustrates their characteristic response. Rheology has been originally developed and focused on synthetic polymers, but it has been extended to the field of natural biopolymers. Here is the typical behaviour of *viscoelastic materials*: most solid materials behave like liquids for long times and most liquids behave like solids for short times; it depends upon the timescale of the rheological experiment. There is a fundamental correlation between rheology and polymer processing. In fact, polymeric materials are always melted in order to be subjected to different manufacturing processes, depending on the type of application. In this regard, rheological properties might help to understand the polymer behaviour when it will be processed.

5.1.1 Melt Flow Index (MFI)

Among rheological analysis, Melt Flow Index (MFI) or mass fluidity index is a polymer rheological parameter experimentally determined to assess the melt viscosity of a thermoplastic material. It is measured as the extrusion rate of a molten polymer flowing through a standard die under the application of a standard weight. MFI might be considered as an indicator of the flowability of the thermoplastic materials (25).

The Melt Flow Index is a rheological property of thermoplastic materials and is inversely proportional to the molecular weight: as the molecular weight rises, there is an increase in the viscosity and thus a decrease in the MFI.
MFI is measured in g/10min: it is determined as the mass in grams of a polymeric material flowing per 10 min. In fact, MFI of a thermoplastic material is defined by a deposition through the melt flow tester at certain standard temperature and load conditions for 10 min.

MFI test is carried out by an instrument called melt flow tester as shown in Figure 27. The instrument typically consists of a cylindrical barrel wrapped and surrounded by a heater coil. The heater is even thermally insulated to minimize heat losses.
A standard weight is applied upon the piston; then the piston head pushes the material through a die. The set-up of the parameters is managed by a control box.

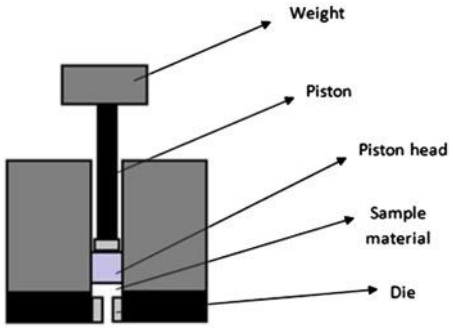


Figure 27 Schematic diagram of a melt flow tester (25)

The reference standard used for Melt Flow Rate (MFR) test is ISO 1133 which establishes the temperature conditions and time interval to be set during the test. ISO 1133-1 provides two test methods: procedure A and procedure B. For the PhD research, method A has been employed to perform the analysis of the three developed compounds. Method A is the method of measuring the mass of the polymer extruded through a die over an established time range.

The test involves a known amount of polymer expressed in grams approximately equal to 5-8 g flowing out of a standard-size capillary die of 2,095 mm diameter and 8 mm length.

The piston is pushed by a standard mass equal to 2,16 kg or 5 kg, depending on the analysed material. Once the molten polymer gets out of the die, the material is taken and weighed on an analytical scale; the MFI is then determined through the control box.

The instrument used in laboratory to measure the MFI of the developed compounds (PLA/PHACT; PLA/ATBC; PLA/PHACT/ATBC) is shown in Figure 28: it is the AMSE MFI-1221 XNR-400 B equipped with an encoder for the piston displacement measurement and an automatic extrudate cutting device.

Through the MFI analysis, the rheological behaviour of the three polymeric compounds have been investigated in terms of processability and suitability for final application. Hence, MFI might be considered as an index of the goodness of the extrusion process depending on molecular structure of the resulting material.

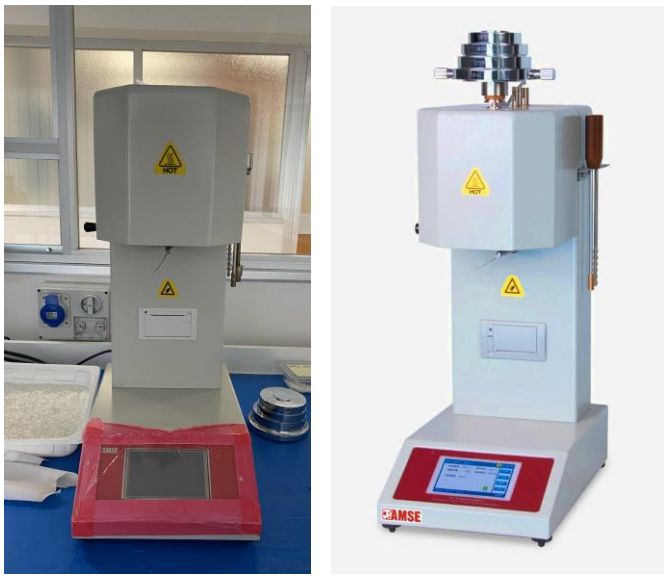


Figure 28 Melt flow tester AMSE MFI-1221 XNR-400 B

Specifically, the laboratory tests were conducted at 190 °C, under the action of a load of 2,16 kg, and samples cutting frequency of 30s. The test has been executed three times for each material. The MFI average results are summarized in Table 8.

Melt Flow Index (MFI)		
Compound	**Conditions**	**Average Value (g/10 min)**
PLA/PHACT	190 °C-2,16 kg- 30 s	5,26
PLA/ATBC	190 °C-2,16 kg- 30 s	33,36
PLA/PHACT/ATBC	190 °C-2,16 kg- 30 s	34,46

Table 8 MFI Avg. Values obtained for the experimental compounds

Regarding PLA/PHACT compound analysis, since the PLA grade used as primary polymeric phase is characterised by an MFI equal to 3 g/10 min at same test conditions (190 °C-2,16 kg), PHACT has correctly improved the melt fluidity of the compound and promoted the extrusion process with a resulting slight increase in the MFI of the final blend.

Regarding PLA/ATBC and PLA/PHACT/ATBC compounds analysis, the use of ATBC and the combined use of ATBC plus PHACT has made the MFI value significantly rising. In this regard, according to Maiza M. et al. (30), plasticizers addition generally increases the polymer chain mobility, leading to a viscosity reduction and consequently to an increased value of MFI. When a smaller amount of citrate ester is added to PLA, the small molecule of citrate penetrates the PLA matrix promoting slipping and sliding. As the amount of the plasticizer increases, more ATBC molecules surround the PLA matrix, reducing furthermore viscosity.

It is worth underline that the two blends tested sharing the amorphous PLA matrix have shown difficult processability during the MFI tests. In fact, the PLA grade used as primary polymeric phase features an amorphous nature and a low MFI value at 190 °C-2,16 kg due to the high D-lactide percentage; for this reason, it has been difficult to perform the tests.

Furthermore, as previously described, both grades of PLA selected for the prototype formulations are suitable for extrusion process and film extrusion. For instance, sheets were produced via cast extrusion and then submitted for the tensile test to perform the mechanical characterization of the materials.

The MFI value of the blends can be increased by using different PLA grades suitable for injection moulding process as well as by the investigation of plentiful process additives that rise polymer MFI, e.g. antioxidants.

5.1.2 Rheometer

Among rheological analysis, a capillary rheometer has been employed to assess the rheological behaviour of the compound PLA/PHACT. The test has been carried out exclusively on this compound since it was already seen from reactive extrusion and Melt Flow Index (MFI) test that the other two formulations PLA/ATBC and PLA/PHACT/ATBC were more difficult to process due to the amorphous PLA grade.
These rheological experiences can be assessed also through Ludovic simulation or similar software. Numerical simulation software for co-rotating twin screw proposes a global analysis of the material behaviour evolution along the process. However, data extracted was not accurate and consistent with experimental experience. Overall, simulation analysis has led to unreliable data not useful to set better theoretical process parameters; consequently, experimental data set was trusted.

Rheological laboratory test is usually performed to provide preliminary information about the material behaviour during extrusion and multiple processes such as injection moulding, blow moulding and film blowing.
Rheometer test helps to simulate manufacturing processes in terms of rheological properties. In fact, capillary rheometers ensure a true simulation of processing conditions by setting proper test parameters, allowing the optimization of the relevant processing data set.

The rheological test of PLA/PHACT compound has been conducted via the CEAST SmartRHEO SR20 advanced instrument supplied by Instron, illustrated in Figure 29, characterised by a maximum force range of 20 kN. This kind of rheometer with twin bore barrel configurations is designed for advanced quality control of thermoplastic materials, as it provides the rheological properties of polymer samples over a wide range of shear rates and testing conditions.

In the twin bore barrel configuration, crosshead with independent load cell on each piston provides superior accuracy, which increases the repeatability of test results.

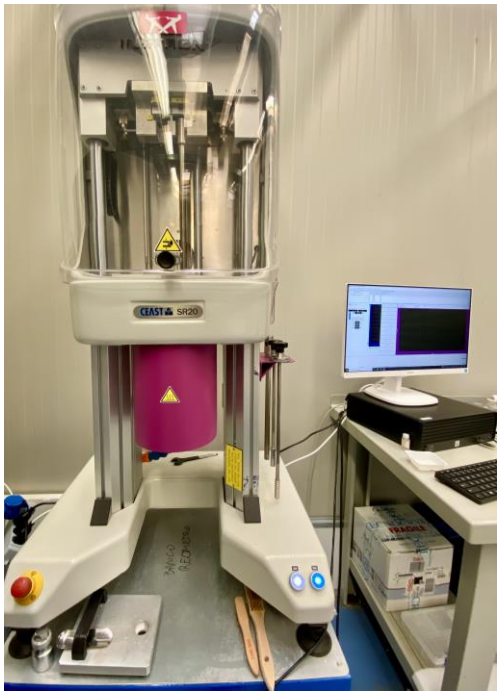


Figure 29 CEAST SmartRHEO SR20 Rheometer

The CEAST SmartRHEO SR20 Rheometer is equipped with a piston system designed to measure the viscosity of polymeric materials as a function of the set temperature and shear rate. The instrument consists of three heating zones and is equipped with pressure transducers (10-200 MPa range) and multiple PT100 temperature sensors which enable to ensure both minimum delay in reaching the test temperature and rapid recovery after sample loading.

To perform the test, about 50 g of material in the form of pellets is introduced into the test chamber, which is heated to the test temperature.

Hence the material from the original granules state becomes molten, it flows out of a cylinder through a capillary mold characterised by 1 mm in diameter, as shown in Figure 30.

Figure 30 Compound PLA/PHACT melt flowing through the capillary mold

For PLA/PHACT rheological test, a compacting force of 300N has been applied during a 300s preheating cycle to ensure homogenous packing and uniform heating of the material. Different shear rate values were set during the test (50-100-150-250-350-500-650-750-850-1.000-1.250-1.500-2.000s-1) as illustrated respectively in Table 9, Table 10, Table 11, from the data extracted through the dedicated software.

	SRre	Viscre	SRap	Viscap	scosity Rabinovic	Pressure
	1/s	Pa*s	1/s	Pa*s	Pa*s	Pa
1	41.741	----	50.000	148.500	177.883	594000.000
2	85.337	----	100.000	71.250	83.493	570000.000
3	130.281	----	150.000	49.500	56.992	594000.000
4	223.854	----	250.000	1368.400	1528.227	27368000.000
5	322.333	----	350.000	1189.929	1292.065	33318000.000
6	480.025	----	500.000	929.025	967.684	37160999.000
7	651.647	----	650.000	783.288	781.308	40730999.000
8	775.387	----	750.000	722.650	698.990	43359001.000
9	908.122	----	850.000	654.765	612.858	44523998.000
10	1128.103	----	1000.000	594.662	527.135	47573001.000
11	1574.091	----	1250.000	512.670	407.116	51266998.000
12	2191.096	----	1500.000	456.975	312.840	54837001.000
13	5282.278	----	2000.000	372.325	140.971	59571998.000
14	5282.278	----	2000.000	375.575	142.202	60091999.000

Table 9 Rheological test data set for PLA/PHACT compound at 170 °C

	SRre 1/s	Viscre Pa*s	SRap 1/s	Viscap Pa*s	scosity Rabinovic Pa*s	Pressure Pa
1	51.762	----	50.000	582.500	562.667	2330000.000
2	107.728	----	100.000	513.750	476.897	4110000.000
3	166.221	----	150.000	459.417	414.582	5513000.000
4	289.109	----	250.000	389.700	336.983	7794000.000
5	418.619	----	350.000	344.607	288.120	9649000.000
6	623.729	----	500.000	285.700	229.026	11428000.000
7	840.796	----	650.000	254.000	196.362	13208000.000
8	991.838	----	750.000	224.717	169.924	13482999.000
9	1147.831	----	850.000	207.868	153.932	14135000.000
10	1391.013	----	1000.000	188.900	135.800	15112000.000
11	1820.828	----	1250.000	170.670	117.165	17066999.000
12	2281.793	----	1500.000	156.217	102.693	18746000.000
13	3302.057	----	2000.000	122.494	74.192	19599001.000
14	3302.057	----	2000.000	121.081	73.337	19372999.000

Table 10 Rheological test data set for PLA/PHACT compound at 180 °C

	SRre 1/s	Viscre Pa*s	SRap 1/s	Viscap Pa*s	scosity Rabinovic Pa*s	Pressure Pa
1	51.150	----	50.000	338.250	330.648	1353000.000
2	105.388	----	100.000	303.875	288.341	2431000.000
3	161.311	----	150.000	277.750	258.274	3333000.000
4	276.828	----	250.000	244.350	220.670	4887000.000
5	396.192	----	350.000	220.179	194.508	6165000.000
6	581.068	----	500.000	194.225	167.128	7769000.000
7	771.906	----	650.000	175.423	147.719	9121999.000
8	902.081	----	750.000	164.150	136.476	9849000.000
9	1034.441	----	850.000	154.059	126.590	10475999.000
10	1236.835	----	1000.000	142.537	115.244	11402999.000
11	1583.751	----	1250.000	127.060	100.284	12706000.000
12	1941.857	----	1500.000	115.700	89.373	13883999.000
13	2689.209	----	2000.000	98.994	73.623	15838999.000
14	2689.209	----	2000.000	96.956	72.108	15512999.000

Table 11 Rheological test data set for PLA/PHACT compound at 190 °C

The output of the rheological test is a Viscosity vs Shear rate graph, showing the trend of apparent viscosity as a function of apparent shear rate.

During the test, data have been collected, managed and elaborated by a dedicated software. At the end of the test, the curves have been obtained by the interpolation of the experimental data and have been processed by the software Origin Pro 8.5, dedicated for graphing and analysis.

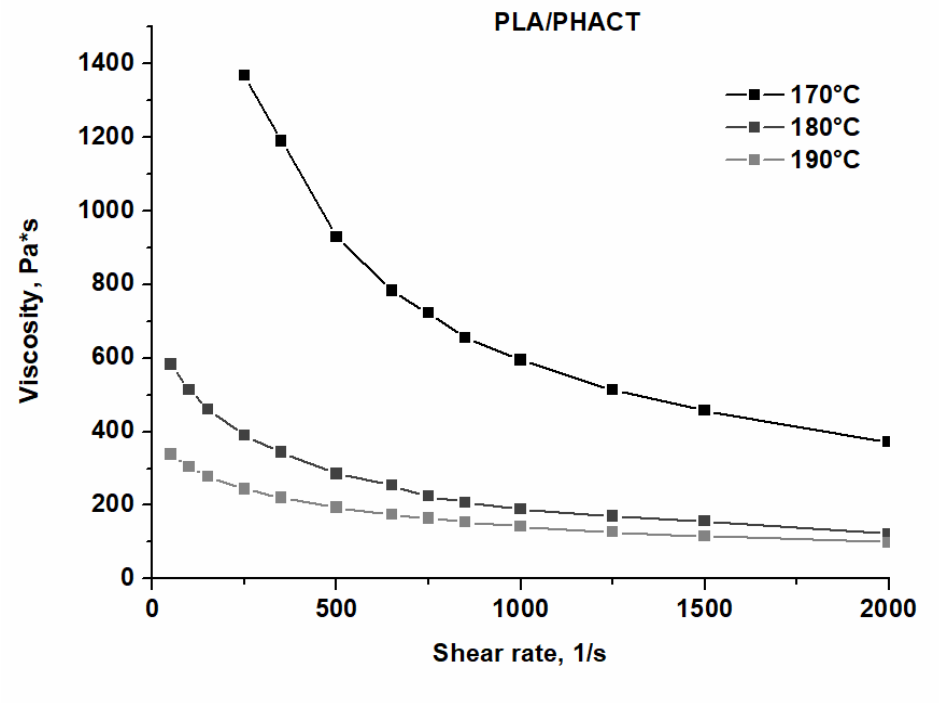


Figure 31 Shear rate vs Viscosity graph for PLA/PHACT compound

The output of the test is the flow curve illustrated in Figure 31: the viscosity (Pa*s) trend of PLA/PHACT compound depending on the shear rate (1/s), as the test temperature changes from 170 to 190°C.

As the curves show, viscosity decreases as the test temperature increases from 170 to 190 °C. The results have also shown that PLA/PHACT exhibits the so-called shear thinning behaviour or the non-Newtonian behaviour of fluids, whose viscosity decreases with increasing shear rate.

5.2 Thermal analysis

5.2.1 Differential Scanning Calorimetry (DSC)

A thermal analysis has been conducted on the prototype compounds via a differential scanning calorimetry (DSC) with the aim to analyse the typical polymeric thermal properties. Actually, DSC analysis allows the thermal and crystallization properties of materials to be evaluated. The test requires small quantity of samples and studies any phenomenon involving a change in the heat capacity of a material, exploring a wide temperature range (29).

The instrument employed to perform the analysis is called calorimeter and measures the heat fluxes associated with thermal transitions occurring in a sample when it is heated/cooled in dynamic conditions. Since heat flow is not an absolute quantity, a reference is needed in order to obtain a differential signal and determine the polymer's behaviour as the output of the test. During the PhD research, a Mettler Toledo DS3 calorimeter with a TC45/100 intracooler system has been used for the DSC analysis; the instrument is shown in Figure 32 a).

Figure 32 a) Mettler Toledo DS3 calorimeter, b) focus on the two crucibles

The calorimeter consists of two sample holders and two crucibles (Figure 32 b): one contains the granule; the other is empty and works as a reference in order to obtain a differential signal. In fact, the empty crucible allows to estimate the amount of heat that must be subtracted to accomplish the sample phase change.

The instrument cell is thermally insulated from the outside and is equipped with two thermocouples used to measure the heat flow from the sample. Specifically, inside the cell, two crucibles are placed respectively on the two thermocouples: as previously explained, the empty one works as a reference and the other contains the sample under test, weighing about 15-25 mg.

To avoid the stagnation of any gases as a melting result, the lid of the crucibles has been perforated. In this way the risk of altering the measurement is avoided and a more homogeneous heat flux to be detected is allowed.

Furthermore, during the test nitrogen, an inert gas, is flushed to ensure the protection of the material from any reactions. In fact, the internal atmosphere of the cell is protected by a nitrogen flow regulated at 50 ml/min.

In polymers field, DSC calorimetry allows to determine different thermal properties when test is performed under dynamic conditions, here is a list of the main ones:

- glass transition temperature (Tg),
- crystallization temperature (Tc),
- melting temperature (Tm),
- enthalpy of fusion (ΔHm) and crystallisation (ΔHc),
- degree of crystallinity (Xc), in case of semi-crystalline polymers.

To manage the thermo-chemical characterization, the Heat-Cool-Heat method was adopted whereby the samples have been subjected to three successive thermal scans: two heating scans (1st heating and 2nd heating) and an intermediate controlled cooling scan (cooling).

The measurement conditions applied during the analysis of the three compounds are listed below:

- Temperature profile: -50 °C to 200 °C,
- Heating rate: 10 °C/min,
- Cooling rate: 10 °C/min,
- Nitrogen rate N_2: 50 ml/min.

Using an analytical scale, one pellet has been taken for each compound (PLA/PHACT; PLA/ATBC; PLA/PHACT/ATBC) and weighted before starting the DSC test, as shown in Table 12.

Compound	Granule weight (mg)
PLA/PHACT	14,3000
PLA/ATBC	22,3000
PLA/PHACT/ATBC	22,5000

Table 12 Samples weight before DSC test

At the end of the DSC tests, data has been collected and analysed by the dedicated software and then has been graphed through Origin Pro 8.5. Particularly, STARe software from Mettler Toledo was adopted to identify the glass transition temperature (Tg), melt temperature (Tm) and melt crystallization temperature (Tc) of the three different compounds components.

A thermogram is obtained showing the trend of heatflow (mW/mg) as a function of temperature (°C). Thermodynamic quantities can be evaluated from the graph analysis.

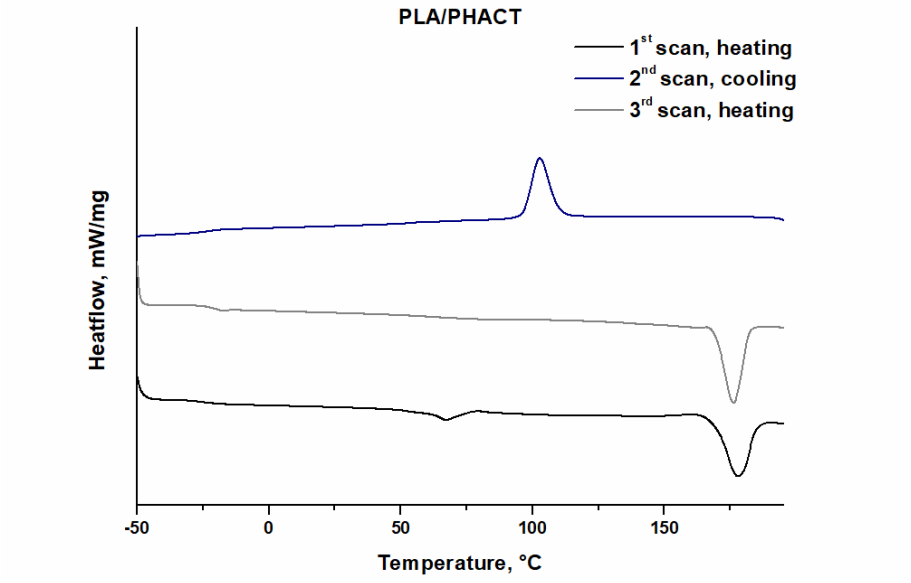


Figure 33 PLA/PHACT compound thermogram

The thermogram of PLA/PHACT is illustrated in Figure 33. From the first heating scan (1st scan) the Tm of PLA has been identified in the peak about 177,4 °C as well as the Tg of PLA at 59,8 °C; furthermore, the Tg of PHACT can be seen at about -30 °C. From the cooling scan (2nd scan) there is a peak of Tc of PLA identified at 103,2 °C. From the second heating scan (3rd scan) the peak of Tm of PLA is visible at 175,6 °C and the PHACT Tg at -23,9 °C.

Regarding the thermograms of the compounds PLA/ATBC and PLA/PHACT/ATBC shown in Figure 34 and Figure 35, two main aspects must be underlined. As previously explained, the PLA grade employed in the two blends features an amorphous nature due to the D-lactide percentage. Moreover, the addition of plasticizers -ATBC in these blends- generally leads to a substantial shift in the characteristic temperatures of the materials. Particularly, the melting peaks of PLA are typically shifted to the left, i.e. lower temperatures, and similarly the glass transition temperatures are strongly shifted to the left. Therefore, ATBC has correctly plasticised PLA. In fact, as described in the previous chapters, literature studies show that when the ATBC rate progressively increases within the PLA blend, Tg and Tm of PLA decrease.

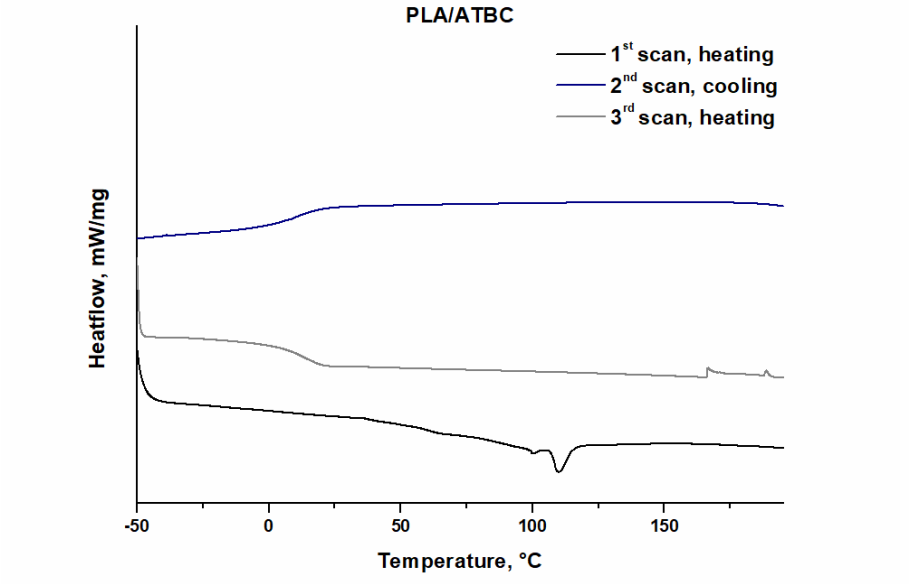


Figure 34 PLA/ATBC compound thermogram

As per literature analysis (30), the use of ATBC in both the blends of PLA is effective in lowering the glass transition temperature Tg, as shown in the related thermograms. On this point, Tg from the 2nd scan of PLA/ATBC compound was observed at 20,3 °C.

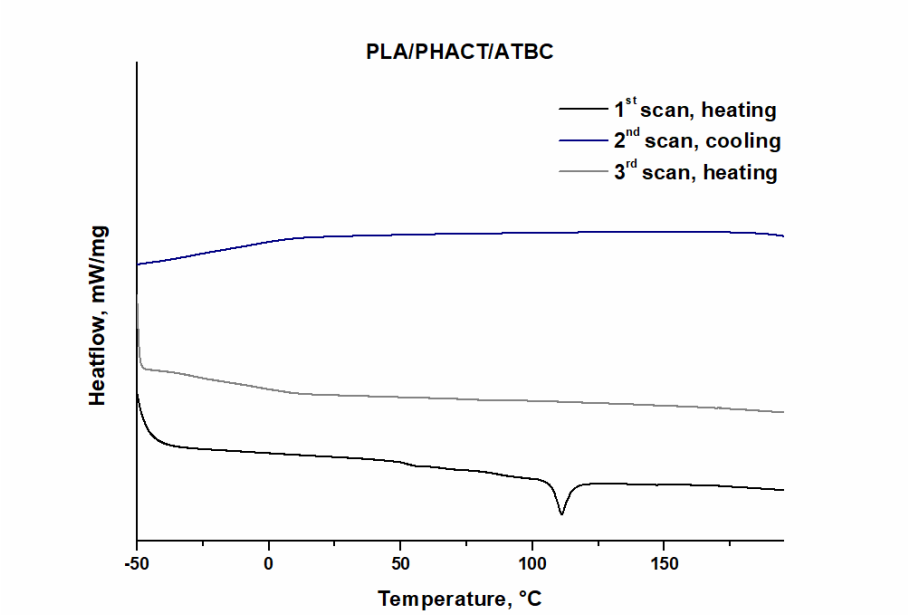


Figure 35 PLA/PHACT/ATBC compound thermogram

According to Maiza M. et al. (30), the addition of a plasticizer in biopolymeric blends leads to an increase in the free volume and consequently to a decrease in the polymer chain interactions. These phenomena determine higher chain mobility at lower temperature: plasticization might be associated with a decrease of the glass transition temperature owing to chain mobility. In fact, the thermal properties of plasticized PLA with ATBC feature lower glass transition temperature (Tg) and melting temperature (Tm) of PLA, as well as lower cold crystallization temperature (Tcc) for semi-crystalline PLA. Furthermore, referring to literature studies related to the effect of plasticizers on the thermal properties of PLA, it was noted that all plasticizers are miscible with PLA thanks to good solubility of PLA in citrate plasticizers. This effect is linked to the polar interactions between the ester groups of the PLA and the plasticizer.

6. Cast extrusion

Cast extrusion is one of the main methods for PLA films and sheets production, characterized by a thickness ≤ 0,076 mm and ≥ 0,25 mm respectively. The process can be synthetized as follows, according to Castro-Aguirre et al: molten PLA is extruded via a lip die and then quenched on polished chrome refrigerated rollers (20).

Polymer sheets and films can be produced using a cast extruder equipped with several boundary elements. The barrel generally includes a single screw equipped with a specific die designed with a thin rectangular shape. The die is located at the head of the extruder by means of an elbow flange and a melt distribution manifold quill. Along the barrel and the die, the temperature profile can be set and adjusted via heating/cooling elements.

The design of the die allows to provide a uniform distribution of speed, pressure, temperature, and molecular orientation. The melt exits from the flat die and then is gradually adjusted to reduce the thickness depending on the film application. The sheet passes through two rollers to reduce and obtain a specific thickness. The two rollers are placed on a movable support whose position can be changed by vertical and horizontal translation via a manual crank system. Then, the film is stretched and cooled until it reaches the pulling system, consisting of an additional pair of counter-rotating rollers. Finally, these rollers pull the film to the winding system.

Cast extrusion parameters can be set and optimized by a dedicated machine software. Furthermore, films can be produced with different methods depending on the reciprocate position of the rollers.

6.1 Minicast 20

The lab-scale cast extruder adopted for the PhD research was MiniCast 20, provided by Eurexma S.r.l., illustrated in Figure 36. It consists of a 20 mm diameter single-screw extruder with an L/D ratio of 30, mounted on a crankcase in which a motor and gearbox are installed. The gearbox output shaft transmits rotation to the screw in the extrusion barrel.

Between the barrel and the gearbox, there is a cylindrical body with a supply nozzle fitted with a cavity for the circulation of cooling air. A volumetric feeding hopper is mounted on the nozzle to dose the plastic granules.

Figure 36 Lab-scale cast extruder Minicast 20

The barrel is heated and cooled along several independent temperature sections, which are automatically controlled through the panel; on this point, temperature is detected during the process via thermocouples.

Minicast 20 is equipped with the so-called *attaccapanni* die, shown in Figure 37. The die allows to achieve a uniform distribution of speed, pressure, temperature and molecular orientation across the width of the sheet and can be manually regulated.

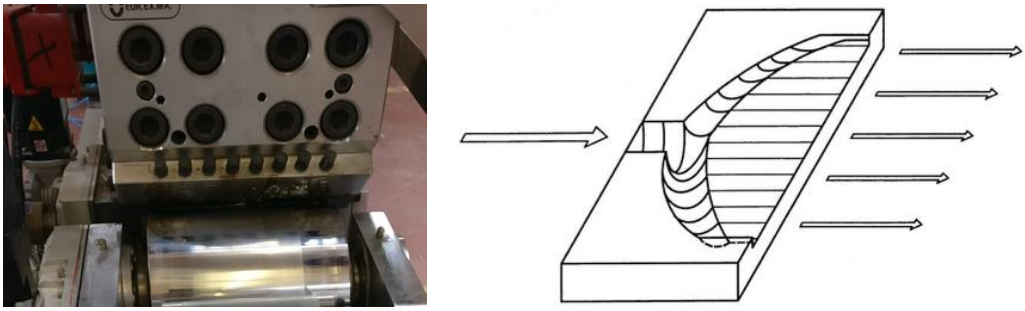


Figure 37 a) Cast extrusion die regulation, b) *attaccapanni* die

The *calender* unit consists of two chromed steel rollers with a diameter of 300 mm. One roller is fixed, while the other can be moved via pneumatic pistons. Furthermore, the rollers are water cooled and their rotation speed can be controlled and regulated. The rollers are mounted on a support whose position can be regulated by means of two cranks that define the horizontal and vertical movement.

Figure 38 Cast extruder *calender* unit: two chrome-plated rollers

The pulling system consists of two counter-rotating cylinders (one chrome-plated and the other rubber-coated), while the winding system includes a rotating cylinder equipped with rubber teeth. In particular, the height of the teeth is adjustable through a pneumatic system with the aid of a compressed air gun to increase the sliding friction coefficient and facilitate the winding. The pulling and winding systems are illustrated below.

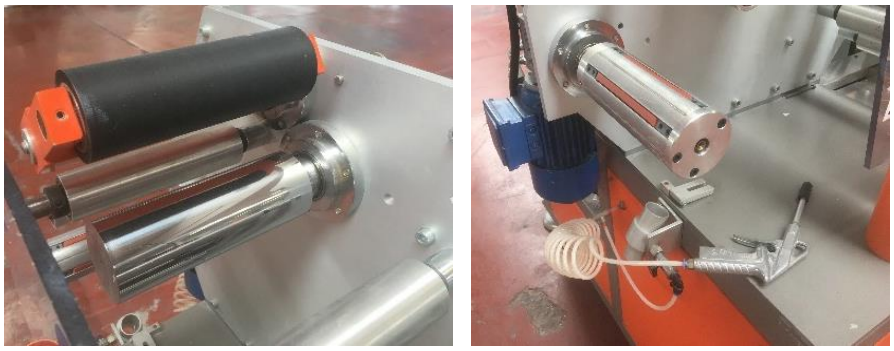


Figure 39 a) Pulling system, b) winding system

Before starting the extrusion process, a dehumidification phase of the compound is usually made. Since biopolymers are mainly hygroscopic materials, pellets dehumidification generally takes place.

Prior to cast extrusion process, the thickness of the die gap and the gap between the rollers is adjusted. Regarding the die gap, it is manually regulated modulating the distance between the upper (fixed) lip and the lower (movable) lip and setting the gap equal to the thickness of the target film. The gap between the rollers is adjusted by modifying the stroke of the pneumatic pistons that move the movable roller, considering a slight smaller thickness to compensate for the effect of swelling. This phenomenon is due to the viscoelastic behaviour of polymers and consists in a partial shape and volume recovery.

Here is a recap of the main machine parameters that can be regulated via the panel during the lab-scale cast extrusion:

- Screw speed: since the hopper is directly connected to the extrusion screw, screw speed indirectly regulates the material flow through the extrusion die.
- Rollers speed: affects the width and thickness of the sheet; specifically, the higher is rollers speed, the thinner is the sheet. Nevertheless, a speed increase might generate a decrease in the width of the sheet.
- Pulling speed: affects the orientation of the polymer chains; in fact, when the pulling speed is higher than the roller one, polymer chains will be stretched and crystallisation will occur due to a mechanical effect. Furthermore, this parameter slightly influences the thickness and the width of the sheet.
- Winding speed: does not affect the quality of the cast extruded sheet but is functional to mechanise the winding.

6.2 Prototype cast extrusion

Cast films have been manufactured via the lab-scale cast extruder Minicast 20 equipped with a 20 mm diameter single-screw extruder. The screw is characterized by a L/D ratio equal to 30 and is equipped with: (i) a volumetric feeding hopper for the pellets introduction into the barrel; (ii) two chromed steel rollers featuring a 300 diameter. The rollers are water-cooled, and their speed can be adjusted and optimized by the controlling panel.

The die is characterized by three individual thermal controlled sections: left, central, right. Processing parameters were manually set and optimized to obtain a thickness of 300 μm for all the three formulations. Pure PLA was first fed in the cast extruder to set a proper temperature profile; afterwards, each compound has been fed.

The barrel and die temperature profiles setting for the cast film extrusion of the three formulations are synthetized in Table 13.

Blend	**T_{gom} (°C)**	**T_{can} (°C)**	**T_{Cil2} (°C)**	**T_{Cil1} (°C)**	**T_{right} (°C)**	**T_{center} (°C)**	**T_{left} (°C)**
PLA/PHACT	175	185	190	190	200	200	200
PLA/ATBC	175	175	170	165	170	165	170
PLA/PHACT/ATBC	175	175	170	165	170	165	170

Table 13 Temperature profile setting for film cast extrusion

For the cast extrusion of PLA/PHACT blend the screw speed was set at 100 rpm; similarly screw speed was set at 110 rpm for PLA/ATBC and PLA/PHACT/ATBC film production. Compounds containing PHACT were difficult to process due to excessive tackiness, which caused severe winding problems of the films. These issues have been overcome using slipping agents and particularly a releasing spray.

The cast extrusion processes and the relative prototype films are shown for the three blends respectively in Figure 40 for PLA/PHACT, in Figure 41 for PLA/ATBC and in Figure 43 for PLA/PHACT/ATBC.

Figure 40 a) PLA/PHACT cast extrusion, b) PLA/PHACT film

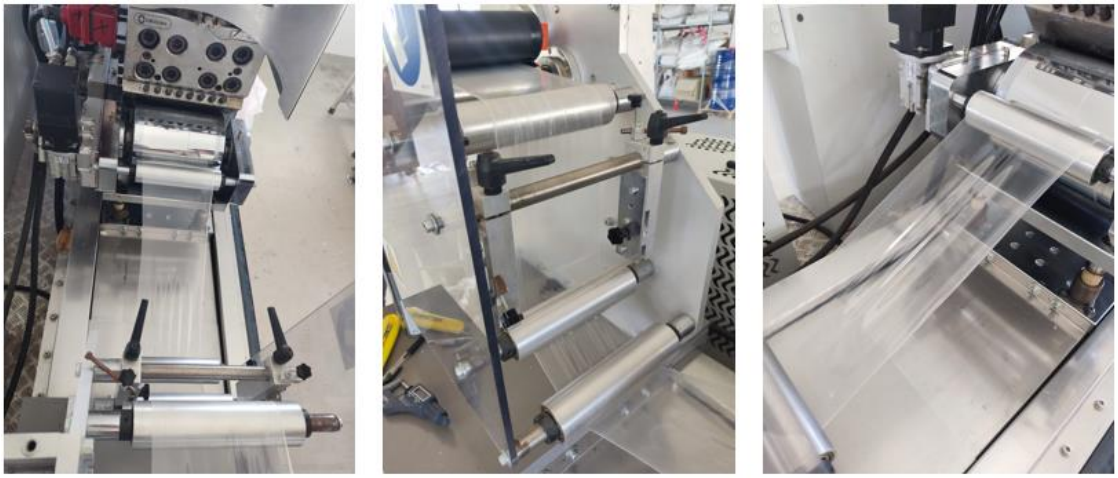


Figure 41 PLA/ATBC cast extrusion

Figure 42 PLA/ATBC optimized cast parameters

When comparing the cast extrusion of PLA/ATBC and PLA/PHACT/ATBC formulations, the PHACT containing blend showed more issues during the process, leading to the production of a film tending to tear and showing uneven thickness, as illustrated in Figure 43.

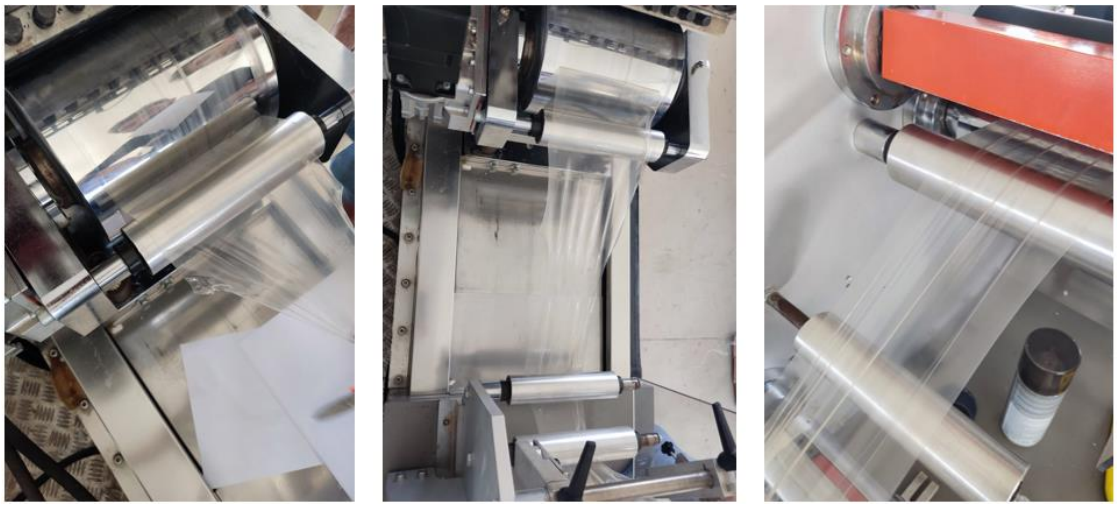


Figure 43 PLA/PHACT/ATBC cast extrusion

7. Film laboratory characterization

Once the cast extrusion of the three formulations PLA/PHACT, PLA/ATBC, PLA/PHACT/ATBC was completed, the mechanical properties of the films have been investigated (elastic modulus, ultimate load, elongation at break, etc.) through the laboratory tensile test. It represents a mechanical test that measures how materials - in this case biopolymeric films- behave when subjected to a force that pulls the specimen until its break. To perform the test, a standard specimen of bioplastic film is attached to a tensile machine that applies an increasing force, recording the stress and the strain until the film breaks.

7.1 Tensile test

During the PhD project, mechanical tests have been conducted in order to carry out a comparative analysis of the mechanical properties of the three formulations both in the machine (MD) and transverse (TD) direction, as reported in Figure 47. Tensile tests have been conducted at room temperature on the standard specimens of the films using the universal testing machine Shimadzu AGS-X with a 5 kN load cell, shown in Figure 44 a.

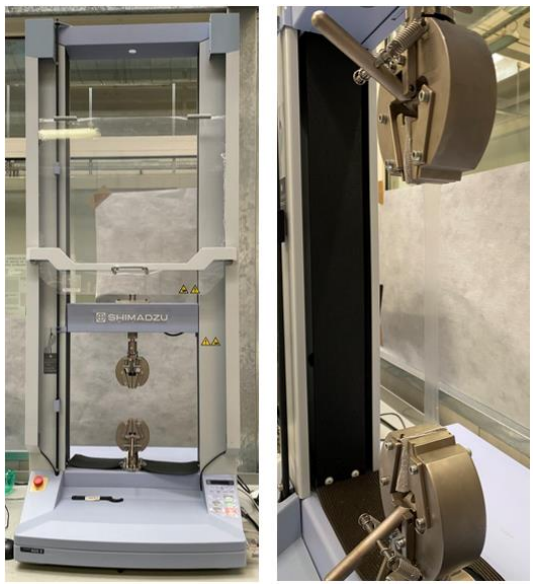


Figure 44 a) Shimadzu AGS-X universal testing machine b) standard specimen

The Standard ISO 527–3 settles the test conditions for determining the tensile properties of plastic films and sheets less than 1 mm thick. The preferred form of test specimen for the determination of tensile properties by this method is a strip that is 10 mm to 25 mm wide and not less than 150 mm long (as shown in Figure 45 and Table 14), having two parallel gauge marks, 50 mm apart, on the central portion of the specimen.

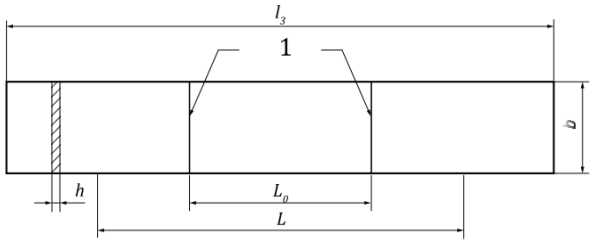


Figure 45 Standard specimen used according to standard ISO 527–3

Dimension	Definition
1	Gauge marks
b	Width: 10 mm to 25 mm
h	Thickness: ≤ 1 mm
Lo	Gauge length: 50 mm ± 0,5 mm
L	Initial distance between grips: 100 mm ± 5 mm
l3	Overall length: ≥ 150 mm

Table 14 Characteristic dimensions of standard specimen according to ISO 527-3

Figure 46 Standard sample dimension of film (PLA/ATBC – MD)

Specimens of the three formulations were cut according to standard dimensions of 150 x 20 mm both in machine (MD) and transverse (TD) direction, as illustrated by way of example in Figure 46. Regarding the film thickness, all samples tested were 300 μm thick.

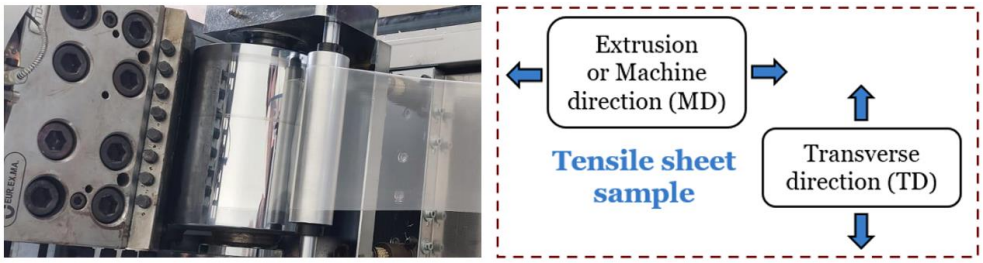


Figure 47 Tensile sheet sample direction: MD and TD

Tensile tests have been iterated on 10 samples of each formulation (5 for MD and 5 for TD): from the individual measurements obtained, the average value of the mechanical quantity of interest has been calculated. Results related to specimens showing mechanical defects have been excluded not to compromise the test.

Overall, cross head speed was set equal to 50 mm/min to carry out the tests of the three formulations both in machine (MD) and transverse (TD) direction. Following the tensile tests, measurements of elasticity modulus E (MPa), maximum load (N), load at break σ_b (MPa) and elongation at break ε_b (%) have been extracted for each sample tested.

Tensile test was first carried out on the lower case studied - PLA/PHACT compound - in order to evaluate the effect of PHACT as a flexible polymeric phase on PLA.

As determined by Luoma E. at al (23) the semi-crystalline grade of PLA shows a brittle nature with the typical mechanical properties illustrated in Table 15, related to film tested according to ISO 527-3.

Mechanical properties	**Typical value**
Tensile modulus	3.500 ± 100 MPa
Tensile strength	50,3 ± 9,3 MPa
Elongation at break	2,5 ± 2,0 %

Table 15 Mechanical properties of semi-crystalline PLA grade

Due to the different PLA matrix used in the three formulations, the stress-strain curves obtained for PLA/PHACT (semi-crystalline PLA) film are separately commented from the other two formulations graphs (amorphous PLA). Indeed, it is worth emphasising that the amorphous nature already provides flexibility and less fragility than the semi-crystalline matrix.

According to Han L. et al. (36), with increasing P3HB4HB content, the brittleness of PLA is improved resulting in a decrease in tensile strength and modulus of the blends. These phenomena are due to the incorporation of the soft elastomeric component in the PLA matrix.

Below the stress-strain curves and the related mechanical properties for PLA/PHACT film are illustrated both in machine (MD) and transverse (TD) direction. From the stress-strain curves, the above-mentioned phenomena can be observed: PHACT improves the elongation at break Ɛb of PLA in both the MD and TD directions. As previously described, PLA is characterized by a brittle nature and an elongation at break Ɛb ≤ 5%. In the MD direction, stress-strain curve shows that the deformation of the material exceeds approximately 60%, thanks to the addition of PHACT which provides ductility to PLA.

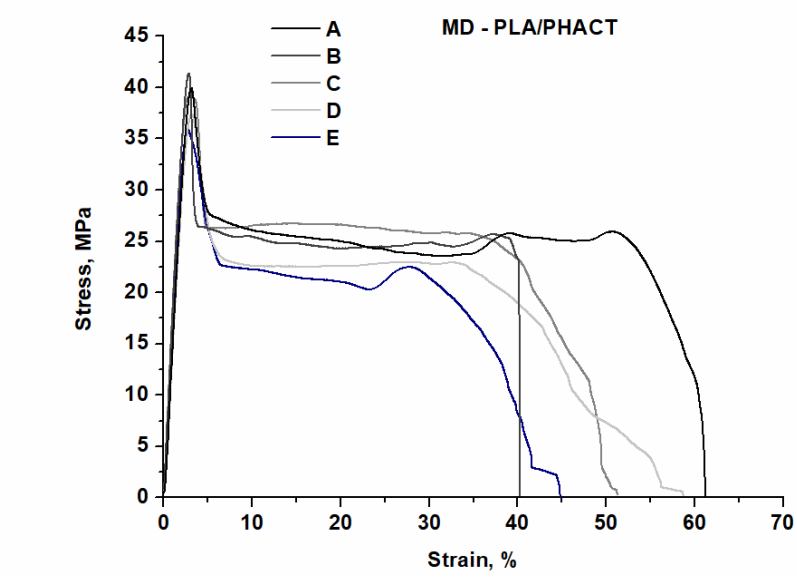


Figure 48 Stress-strain curve: MD-PLA/PHACT

PLA/PHACT - MD	E (MPa)	Max Load (N)	σ_b (MPa)	ε_b (%)
Test MD-A	1.785,58	126,98	39,93	61,27
Test MD-B	1.932,87	106,74	41,37	40,28
Test MD-C	2.101,45	108,09	39,16	51,29
Test MD-D	1.756,17	123,38	37,39	58,75
Test MD-E	1.849,81	109,72	35,86	44,85
Average	**1.885,18**	**114,98**	**38,74**	**51,29**

Table 16 Tensile test mechanical properties of the film MD - PLA/PHACT

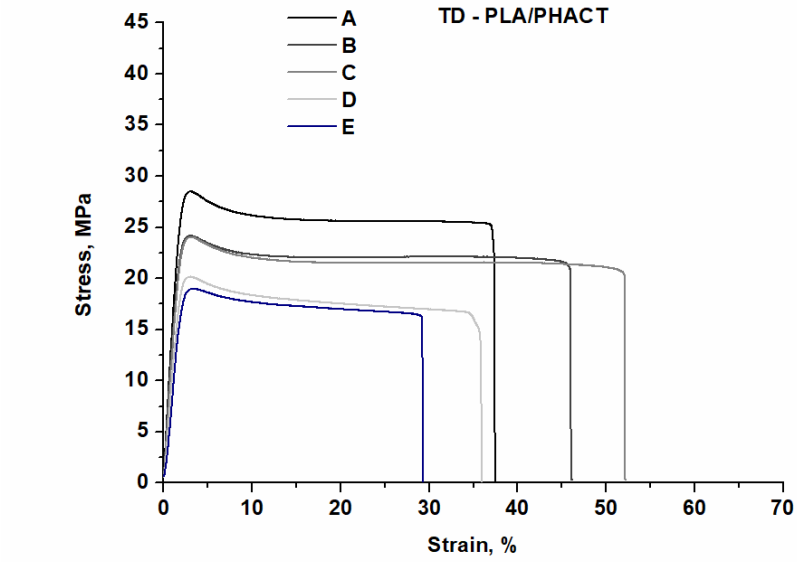


Figure 49 Stress-strain curve: TD-PLA/PHACT

PLA/PHACT - TD	E (MPa)	Max Load (N)	σ_b (MPa)	ε_b (%)
Test TD-A	1.582,30	75,23	28,49	37,48
Test TD-B	1.535,80	66,71	24,17	46,16
Test TD-C	1.425,48	76,42	24,03	52,21
Test TD-D	1.198,77	50,80	20,16	35,97
Test TD-E	1.092,67	45,56	18,98	29,32
Average	**1.367,00**	**62,94**	**23,17**	**40,23**

Table 17 Tensile test mechanical properties of the film TD - PLA/PHACT

Since the two formulations PLA/ATBC and PLA/PHACT/ATBC share the same polymeric matrix of amorphous PLA, the stress-strain curves and related mechanical properties will be compared in both MD and TD as follows. As described by Coltelli M-B. et al. (33), the addition of ATBC generates a decrease in the tensile modulus and an increase in the strain at break due to the plasticizer effect.

From the analysis of the stress-strain measurements, PLA/ATBC formulation exhibited in MD direction a very high elongation at break > 1.000%, revealing very similar trend for all the specimens tested. This trend was also similar in TD direction: the curves reached a very high value: Ɛb > 950% approximately.

Figure 50 PLA/ATBC tensile test: a) start, b) elongation at break; c) after break

As illustrated in PLA/PHACT/ATBC stress-strain curves, the addition of PHACT within a PLA/ATBC blend has led to a decrease in stress at break in both MD and TD directions. The curves have also shown a very high elongation at break of the material in MD direction (Ɛb) similar to PLA/ATBC formulation; whereas, focusing on TD direction, PLA/PHACT/ATBC has exhibited a less flexible nature compared with PLA/ATBC.

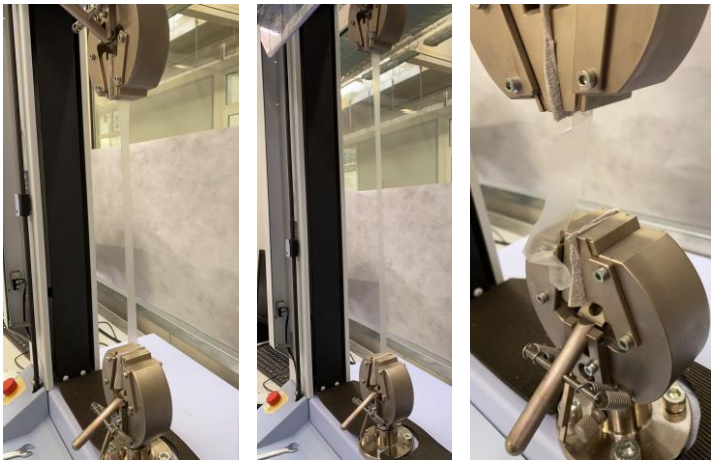


Figure 51 PLA/PHACT/ATBC tensile test: a) start, b) max elongation, c) after break

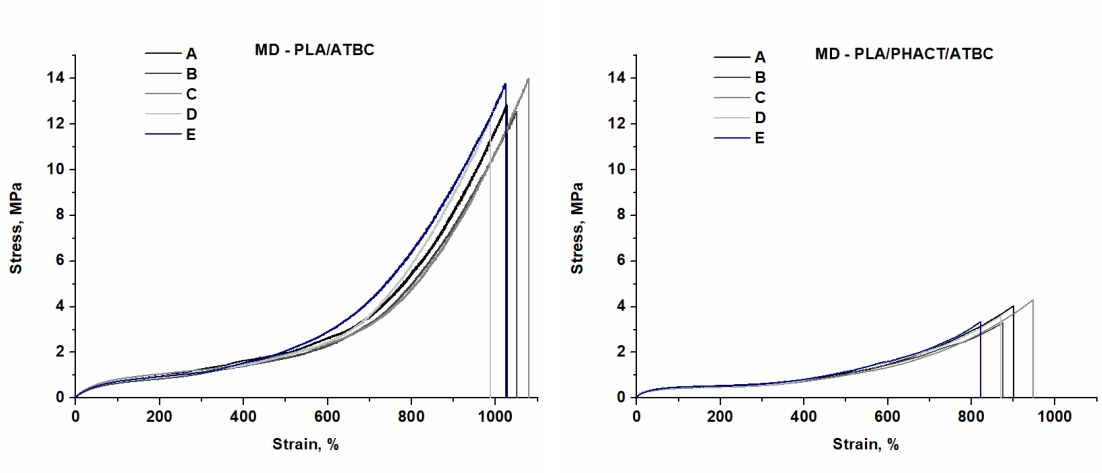


Figure 52 Stress-strain curves: a) MD-PLA/ATBC, b) MD-PLA/PHACT/ATBC

PLA/ATBC - MD	E (MPa)	Max Load (N)	σ_b (MPa)	ε_b (%)
Test MD-A	4,09	77,42	12,90	1.028,20
Test MD-B	3,63	75,48	12,58	1.050,95
Test MD-C	4,32	84,05	14,01	1.079,35
Test MD-D	4,07	73,52	12,25	988,40
Test MD-E	4,11	82,64	13,77	1.024,74
Average	**4,04**	**78,62**	**13,10**	**1.034,33**

Table 18 Tensile test mechanical properties of the film MD - PLA/ATBC

PLA/PHACT/ATBC - MD	E (MPa)	Max Load (N)	σ_b (MPa)	ε_b (%)
Test MD-A	1,23	24,19	4,03	900,74
Test MD-B	1,02	19,80	3,30	875,80
Test MD-C	1,35	25,83	4,31	948,67
Test MD-D	1,11	21,59	3,60	871,14
Test MD-E	1,27	20,06	3,34	822,61
Average	**1,20**	**22,29**	**3,72**	**883,79**

Table 19 Tensile test mechanical properties of the film MD - PLA/PHACT/ATBC

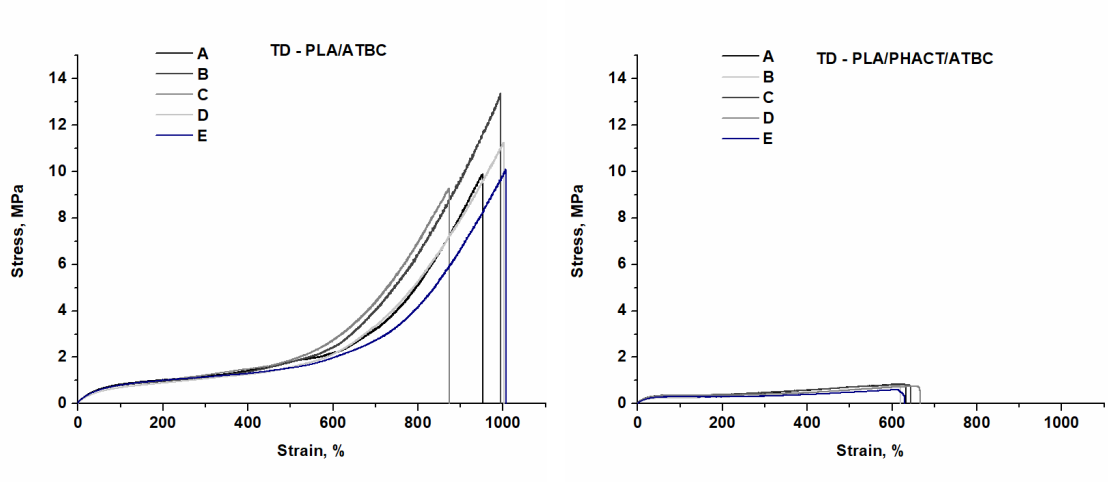


Figure 53 Stress-strain curves: a) TD-PLA/ATBC, b) TD-PLA/PHACT/ATBC

PLA/ATBC - TD	E (MPa)	Max Load (N)	σ_b (MPa)	ε_b (%)
Test TD-A	3,50	59,46	9,91	953,51
Test TD-B	4,24	80,35	13,39	994,39
Test TD-C	3,22	55,74	9,30	874,04
Test TD-D	3,43	67,64	11,27	1.002,56
Test TD-E	3,41	60,72	10,12	1.007,08
Average	**3,56**	**64,78**	**10,80**	**966,32**

Table 20 Tensile test mechanical properties of the film TD - PLA/ATBC

PLA/PHACT/ATBC - TD	E (MPa)	Max Load (N)	σ_b (MPa)	ε_b (%)
Test TD-A	2,36	5,08	0,85	632,31
Test TD-B	1,52	4,50	0,75	620,17
Test TD-C	2,56	4,88	0,81	644,27
Test TD-D	2,27	4,51	0,75	666,59
Test TD-E	1,90	3,61	0,60	629,54
Average	**2,12**	**4,52**	**0,75**	**638,58**

Table 21 Tensile test mechanical properties of the film TD - PLA/PHACT/ATBC

Following the comparison of the above results, PLA/ATBC blend has performed as an elastomer, showing a high elongation at break comparable to PLA/PHACT/ATBC but with a complete elastic recovery.

PLA/PHACT/ATBC curves have shown that combined use of plasticizer and ductile secondary polymeric phase leads to an increase in elongation at break and a decrease in tensile strength and elastic modulus. On the other hand, PLA/ATBC has revealed an extra outstanding feature: a higher stress at break both in MD and TD directions, proving more resistance. This behaviour was also found by a qualitative tensile test conducted on the filaments of both formulations: a greater manual force had to be applied to pull the PLA/ATBC filament than the one required to stretch the PLA/PHACT/ATBC filament.

In the light of the above considerations, the Life Cycle Assessment (LCA) analysis described in the following chapter has been conducted on PLA/ATBC formulation as the most promising blend of the PhD research to match the designed purpose. In fact, PLA/ATBC has shown perfect transparency and a complete elastic recovery; thus, ATBC has correctly plasticized PLA matrix. The blend behaves as an elastomer because, when stretched, shows a high elongation and then, when the force is released, returns to its initial position with minimal residual strain. Last but not the least, in line with the purpose of the thesis, it is biodegradable and compostable at the end-of-life. For the above-mentioned considerations, PLA/ATBC might be considered a bio-elastomer with a high degree of innovation and technological content.

Following the above discussion, a qualitative comparison between mechanical properties of standard EPDM rubber and the prototype blends PLA/ATBC and PLA/PHACT/ATBC is shown in Table 22. It is worth underlining that EPDM standard values have been collected from typical datasheet and companies' websites, but both elongation at break and tensile strength may vary according to different hardness, composition and final application of the rubber. Regarding the bio prototype blends, both elongation at break and tensile strength at break, respectively ε_b and σ_b, have been taken from the tensile tests results previously described, both in MD and TD directions. The standards generally adopted for tensile tests are different between rubber and thin plastic films: for the first one ISO 37 is generally used, while for thin sheets ISO 527-3. Nevertheless, the mechanical comparison provides an estimation of order of magnitude.

Mechanical properties	**EPDM**	**PLA/ATBC**	**PLA/PHACT/ATBC**
Elongation at break (%)	300-600	990-1.080 MD 870-1.000 TD	820-950 MD 620-660 TD
Tensile strength (MPa)	7-21	12-14 MD 9-13 TD	3-4 MD 0,6-0,9 TD

Table 22 Mechanical comparison between EPDM and prototype blends

Along with mechanical properties, here is a qualitative comparison of thermal properties. Operational temperature values for EPDM fall within a range of -50 °C and +130 °C. However, the range itself can vary depending on the curing systems and final product boundary conditions.

With regard to the prototype formulations, PLA/ATBC featuring an amorphous nature has shown a Tg about 20 °C, due to the plasticization effect induced by ATBC, as illustrated in the thermal analysis conducted in Chapter 5.2.1. Moreover, temperature profiles set for lab-scale extrusion might be used as a reference to estimate materials processing performance.

8. Life Cycle Assessment (LCA)

Life Cycle Assessment or LCA is a methodology that allows a quantitative and analytical environmental impact assessment of a product or process by analysing the entire value chain from raw materials selection to disposal and waste treatment.

Internationally, the LCA methodology is regulated by the ISO 14040 series of standards that rule the life cycle assessment involving four steps of study to ensure analysis repeatability, as described by Fonseca A. et al. (59):

- **Goal and scope definition**: to define the objectives and aim of the analysis;
- **Life Cycle Inventory (LCI)**: to compile an inventory of system inputs and outputs during the life cycle;
- **Life Cycle Impact Assessment (LCIA)**: to study the potential environmental impact related to the inputs and outputs previously outlined;
- **Life Cycle Interpretation**: to understand and evaluate the results.

In essence, LCA methodology enables the identification, quantification and evaluation of environmental and energy loads of a production system throughout its life cycle. LCA quantitative nature is one of its outstanding properties; in this regard, environmental impacts evaluation is based on cause-effect models (60).

According to Suwanmanee U. et al. (48), LCA represents one of the most adopted methods to evaluate products environmental impacts, since the analysis allows to quantify the potential environmental impact related to each life cycle stage of products. Specifically, Ramesh P. and Vinodh S. (58) define the typical life cycle of a product as the following steps: (i) raw materials extraction and processing; (ii) manufacturing; (iii) use; (iv) disposal.

The PhD LCA analysis has been made following the above-mentioned methodology. To perform the calculation, SimaPro 9.3 software developed by PRé Consultants has been used, specifically the release 9.3.0.2.

8.1 Goal and scope definition

The aim of the analysis is to perform a comparative Life Cycle Assessment between two different sets of o-rings for automotive applications, made respectively from a traditional fossil-based elastomer -Ethylene Propylene Diene Monomer (EPDM)- and from the promising prototype bio-elastomer PLA/ATBC.

Here is a recap of the main features of EPDM (Figure 54) which explain its broad usage as an o-ring: wide working temperature range lets EPDM to be employed both at low temperatures (-40/-60 °C) and high temperature (about 130 °C). Moreover, EPDM boasts ageing resistance (including weathering, ozone, sunlight, heat and water resistance) as well as chemical and steam resistance. However, this elastomer is completely fossil-based and is not nearly recycled at the end-of-life.
As described by Vlasopoulos A. et al. (51), plastic waste is extremely hard to decompose, hence causes long-lasting environmental impact.

Figure 54 Typical EPDM o-rings (from SJK seal website)

Fucntional unit definition

One of the first LCA analysis steps is the functional unit definition: a quantitative reference factor to which all input and output data can be normalized. The primary purpose of the functional unit is to enable comparability of LCA results.
The functional unit is used when the systems under evaluation show different features and a comparison on a common basis must be ensured. After the functional unit selection, the reference flow can be determined to define the product amount required to model it. For this LCA study, the functional unit used is 1 kg, specifically expressed as the production of 500 o-rings of 2 g each.

It has been assumed for the analysis that a small standard sized o-ring weights 2 grams regardless of the material and considering the similar density of EPDM and PLA: respectively 1,3 and 1,24 g/cm^3.

The reference flow to fulfil the functional unit is schematically quantified in Table 23.

Fossil-based elastomers	**Bio-elastomers**
500 o-rings made of EPDM	500 o-rings made of PLA/ATBC
o-ring weight of 2 g	o-ring weight of 2 g

Table 23 Reference flow of the analysed systems

In essence, this analysis aims to compare the Life Cycle of an innovative compostable elastomer with a conventional one. The industrial field is that of automotive, considering among possible applications: brakes, suspensions, power steering, electrical components, etc.

System definition and boundaries

A further focus of the analysis provides the delineation of the system boundaries (physical boundaries), which must be consistent with the scope set at the study initial stage. Boundaries can be defined according to the following three approaches: (i) cradle-to-gate; (ii) cradle-to-grave; (iii) cradle-to-cradle:

- Cradle-to-gate: evaluates a product life cycle by including all the activities before its usage (from raw material extraction phase to the exit from plant) and does not consider the disposal scenario.
- Cradle-to-grave: examines all environmental loads linked to a product system. It consists of a comprehensive analysis that evaluates impacts from the raw material extraction, the production, the distribution and usage up to its end-of-life stage disposal.
- Cradle-to-cradle: can be compared to a complete cradle to grave analysis in which recycling processes replace the end-of-life disposal phase. This production system is closed and allows to minimize environmental impacts, since it provides end-of-life recycling, without generating waste but reintegrating the closed cycle.

Apart from the physical boundaries, other categories should be outlined:

• Time boundaries: identify the time interval in which the potential impacts of the product or service are evaluated. However, few elements of the system may evolve over time and therefore should be averaged throughout a defined time interval.

• Geographical boundaries: geographical contexts can significantly affect the results, as a wide range of different data might be used for certain processes. One of the main examples is the energy production.

• Technological level: besides temporal and geographical boundaries, the level of technology assumed for the analysis should be determined.

Regarding the PhD research, the LCA analysis has been performed on *cradle to grave* systems. Therefore, the raw material production was included in the system, as well as the waste disposal; while the system geographical boundaries have been located in Italy, selecting for instance Italian companies. As far as time is concerned, the current time scenario has been chosen together with the current technological level.

Besides the different raw materials production (from fossil sources for EPDM against bio-derived for PLA/ATBC), reactive extrusion and injection moulding are common manufacturing technologies for the two elastomers.

Nevertheless, the blends feature different disposal, considering the different treatment split among the end-of-life scenarios. On this point, EPDM diverges from PLA/ATBC for the composting end-of-life scenario, which is clearly typical only for biodegradable and compostable materials.

Despite the PhD research has focused on the cast extrusion process to make a complete mechanical characterization of the prototype material, injection moulding has been selected as the second manufacturing step in the LCA analysis. In fact, injection moulding might be considered one of the most representative technologies for the o-ring production on industrial scale. In light of the above considerations, a schematic representation of the LCA systems boundaries is provided in Figure 55.

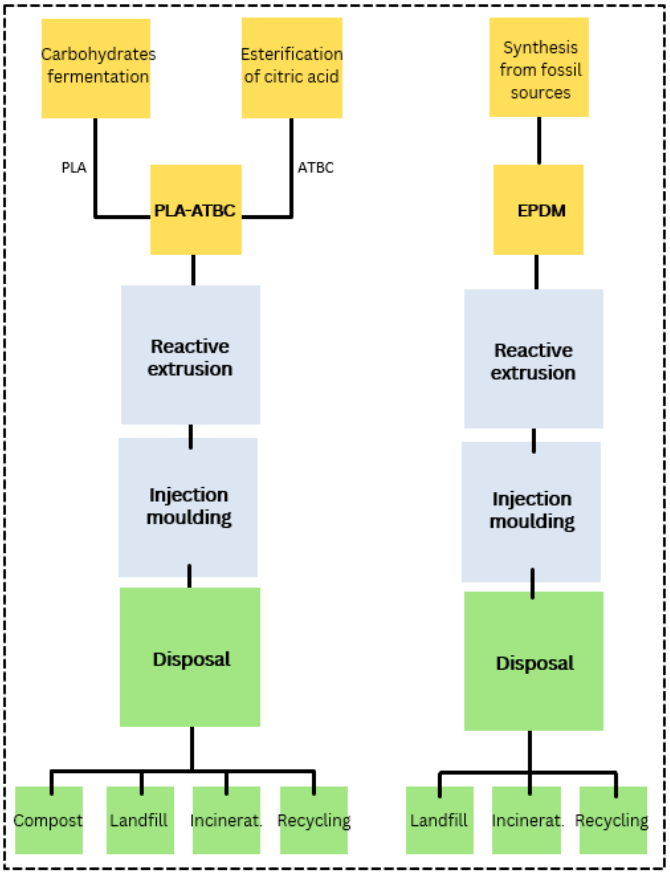


Figure 55 LCA flowchart and system boundaries

For the LCA analysis, a software is usually needed to process a large amount of data. In this sense, SimaPro 9.3 has been adopted for the LCA analysis since it enables the collection and evaluation of data about products environmental impact. Among the wide range of analysis, the software allows to extract sustainability reports and to identify performance indicators in accordance with ISO 14040 and ISO 14044. Respectively, ISO 14040 (2006) is about the Environmental management–life cycle assessment, life cycle assessment–principles and framework; while ISO 14044 (2006) is about the Environmental management–life, cycle assessment–life cycle assessment–requirement and guideline.

On this point, SimaPro includes lots of libraries containing a large amount of data periodically updated and collected from reliable sources.

Among the several databases, the input and output information regarding materials, processes, as well as their disposal can be found.

Here is a recap of the main SimaPro databases:

- Agri-footprint: collects input and output data of the main processes and materials regarding agriculture and animal husbandry as well as food: it includes data on crops, animal production systems, transport, production and usage of fertilisers.
- Ecoinvent 3: collects data from a wide range of sectors, such as energy production, transportation, chemical production, metals, plastics, building materials and agricultural products. In SimaPro there are six versions of the same database characterised by three different data processing modes and two possible process types. The entire database has over 20.000 interconnected datasets, each describing a life cycle inventory in terms of process.
- EU & DK Input Output Database: includes data from the European Union and Denmark, as well as additional sources on raw materials and derivatives, energy supply, transport and waste management. Each set of information has been approved by the industrial associations.
- Industry data 2.0: gathers data on industrial processes and production statistics collected from industry associations, such as Plastics Europe, World Steel, ERASM and IMOA.
- Methods: includes a set of pre-defined impact assessment methods that are significant to achieve the LCA results.
- USLCI: gathers LCI data on agricultural and industrial processes in the U.S.

8.2 Life Cycle Inventory

For the LCA calculation the so-called Cut-off approach has been adopted to deal with the different waste treatment scenarios. According to Meys R. et al. (41), the Cut-off approach might be considered as a worst-case allocation for rubber products, since it assumes that no environmental impact is allocated to the results of waste treatment, but to the products subjected to the analysis.
For the analysis, the Ecoinvent 3 database has been used for most inputs and outputs. Furthermore, data has been concatenated: disposal was outlined within the material production process to create a unique flow: from production to extrusion and injection moulding till distribution.

PLA has been selected from Ecoinvent 3 database; 1 kg of PLA has been figured as: Polylactide, granulate {GLO}| production| Cut-off, U.

However, when the input/output inventory information was not available in Ecoinvent 3 database, information was studied and adopted from literature to complete the analysis. In this regard, EPDM has been assumed as a synthetic rubber (Figure 56) as per literature studies.

EPDM has been selected from Ecoinvent 3 database; 1 kg of EPDM has been figured as: Synthetic rubber {RER}|production| Cut-off, U.

Rubber membrane	synthetic rubber production | synthetic rubber | Cutoff, S	this module refers to the EPDM elastomer as it is used in technical products. The name "rubber" means only the unvulcanised polymer without any fillers. EPDM is one of many different rubbers and there are EPDM elastomers of many different compositions, here average values are taken, Europe manufacture

Figure 56 EPDM inventory

Instead, **ATBC** has been defined and created as a new material in SimaPro, making use of the scientific paper and the major inventory items for ATBC shown in Figure 57.

Table 8 Major inventory items for Acetyltributylcitrate (based on PEF documentation)

Item	Quantity	Unit	Provider
Input			
1-butanol	0.61	kg	Market for 1-butanol | 1-butanol | Cutoff, U—GLO
Acetic acid	0.17	kg	Market for acetic acid, without water, in 98% solution state | acetic acid, without water, in 98% solution state | Cutoff, U—GLO
Citric acid	0.53	kg	Citric acid production | citric acid | Cutoff, S—RER
Electricity, medium voltage	0.14	kWh kg^{-1} ATBC	Market group for electricity, medium voltage | electricity, medium voltage | Cutoff, U—Europe without Switzerland
Heat, from steam, in chemical industry	0.44	MJ	Market for heat, from steam, in chemical industry | heat, from steam, in chemical industry | Cutoff, U—RER
Tap water	1	kg	Market for tap water | tap water | Cutoff, U—Europe without Switzerland
Chemical factory, organics	4E-10	Items	Market for chemical factory, organics | chemical factory, organics | Cutoff, U—GLO
Transport, freight train	0.79	t*km	Market for transport, freight train | transport, freight train | Cutoff, U—Europe without Switzerland
Steam, in chemical. industry	0.13	t*km	Market for transport, freight, lorry > 32 metric ton, EURO6 | transport, freight, lorry > 32 metric ton, EURO6 | Cutoff, U—RER
Output			
ATBC	1	kg	
Municipal solid waste	0.056	kg	Treatment of municipal solid waste, sanitary landfill | municipal solid waste | Cutoff, U—CH
Municipal solid waste	0.056	kg	Treatment of municipal solid waste, incineration | municipal solid waste | Cutoff, U—CH
Wastewater, average	0.2/1000	m^3	Market for wastewater, average | wastewater, average | Cutoff, U—Europe without Switzerland

Figure 57 ATBC inventory based on PEF documentation (38)

Once defined the raw materials, the blend PLA/ATBC has been represented as a unique material in SimaPro, according to the constituents' ratio established by the formulation.

Regarding the manufacturing processes, they have been defined for EPDM and PLA/ATBC as {RER}|Cut-off, U both for extrusion of plastic and injection moulding.

On distribution evaluation, o-ring freight has been assumed to be the same around Italy for the two materials. In this sense, the following Italian cities have been chosen as freight destinations to cover the whole country o-rings distribution. Here is a recap of the selected cities and the calculated distances from the production plant called Franplast S.p.A. chosen as reference and sited in Brescia:

- Brescia-Milano: 100 km,
- Brescia-Pomezia: 600 km,
- Brescia-Brindisi: 1.000 km.

Freight has been assumed to be the same for EPDM and PLA/ATBC o-rings in order to underline the environmental impact differences generated, limiting the boundary conditions.

Regarding the waste disposal scenarios and the related freight distances, the following Italian companies have been selected for the analysis.
The same treatment plants have been assumed for EPDM and PLA/ATBC o-rings, since they share the same disposal scenarios except for composting.
Here is a list of the Italian companies assumed for the study:

- Franplast S.p.A.- o-ring production;
- Gianeco S.r.l.- recycling plant;
- A2A Brescia - waste incinerator;
- Systema Ambiente S.r.l.-Bagnolo Mella – composting plant;
- Systema Ambiente S.r.l. – disposal plant.

In addition, assuming the production company as a collection centre, disposal scenarios distances have been calculated between the reference production plant (as a collection centre) and the waste treatment plants. This approach is valid for both materials.

Within SimaPro, freight has been defined the same for the two formulations via road transport as here described:

Transport, freight, lorry 3.5-7.5 metric ton, EURO5 {RER} transport, freight, lorry 3.5-7.5 metric ton, EURO5| Cut-off-U.

Regarding waste disposal scenarios, traditional polymers and biodegradable materials generally share three alternatives: landfill disposal, incineration and recycling. Indeed, EPDM and PLA/ATBC share the above-mentioned three options.

In addition, bio-polymers provide even composting: this alternative is only possible for materials featuring characteristics of biodegradability and compostability.

In Table 24 a scheme of the different end-of-life scenarios split that has firstly been assumed for the study.

Disposal scenario	EPDM	PLA/ATBC
Recycling	2%	3%
Incineration	88%	15%
Landfill	10%	25%
Composting	-	57%

Table 24 Disposal scenario split for EPDM and PLA/ATBC

Regarding EPDM, the recycling ratio has been assumed equal to 2% since according to Chittella H. et al. the ratio of recycling and reuse of general rubber goods reaches only 1.5% of the total amount of waste generated (42). Landfill split has been outlined as 10%, aiming at the EU target of landfill reduction to no more than this rate for municipal waste by 2035.

Focusing on PLA/ATBC, the composting ratio has been taken from Biorepack data which determined the Italian rate reached in 2023 equal to 56,9% (44). Biorepack is the national consortium for compostable bioplastic packaging, representing the sector within the CONAI system, described in the next paragraphs.

Other waste disposal ratios have been hypothesised on the basis of experience on different studies. With regard to waste disposal treatment, some assumptions have been made from the LCA experience and the scientific literature review. Therefore, some data were taken from the SimaPro libraries, others were entered and created into the system based on literature articles and experience. Here is a recap of disposal treatments respectively for EPDM and PLA/ATBC o-rings.

EPDM disposal assumptions:

Landfill: among the different inputs, the freight from consumer to collection point and from collection point to landfill should be considered. However, in this thesis the freight was suggested to be the same for both materials analysed.

Hence disposal scenarios distances have been calculated only between the reference production plant (as a collection centre) and the waste treatment plant. For instance, the distance production plant-landfill is about 30 km.

Transport has been considered to be by road and with full load (LF) as follows:
Transport, truck <10t, EURO5, 100% LF, default {GLO} Economic, U

Based on scientific literature data (50), the landfill output emissions for 1 kg of Polyethylene terephthalate (PET) or polypropylene (PP) are equal to 1,2 kg of CO_2 and 0,024 kg of methane.
For 1 kg of EPDM air emissions have been assumed equal to PET/PP outputs, as shown in Figure 58.

Output noti a tecnosfera. Prodotti evitati		Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Input								
Input noti da natura (risorse)	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Input noti da tecnosfera (materiali/combustibili)		Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	
Transport, truck <10t, EURO5, 100%LF, default {GLO} Economic, U		30	kgkm	Non definito				
(Inserisci linea qui)								
Input noti da tecnosfera (elettricità/calore)		Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Output								
Emissioni nell'aria	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
Methane		0,024	kg	Non definito				
Carbon dioxide		1,2	kg	Non definito				
(Inserisci linea qui)								
Emissioni in acqua	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Emissioni nel terreno	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Flussi dei rifiuti finali	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Emissioni non materiali	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Temi sociali	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								
Temi economici	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento

Figure 58 Landfill disposal for 1 kg of EPDM

Incineration: this disposal method contributes to the reduction of waste volumes reducing pressure on landfills (46). For the PhD analysis, energy recovery calculation has been considered: heat output to technosphere has been added as an avoided product in SimaPro model. The heat produced during incineration has been calculated considering the calorific value of EPDM assumed to be 35 MJ/kg (a mid-value between 30-40 MJ/kg) and the weight of the material. A plant efficiency of 75% has been considered. Transport inputs were assumed equal to disposal ones, varying the distance according to the incineration centre.

Regarding the outputs, emissions to air (Carbon dioxide, Carbon monoxide, NMVOC, non-methane volatile organic compounds, Particulate matter, less than 10 μm, Heat, lost, Nitrogen dioxide, Ammonia, Hydrogen chloride, Hydrogen fluoride, Sulphur dioxide) have been considered, assuming PET data (50).

Along with emissions to air, known outputs to technosphere upon treatment (non-hazardous waste, ash and slag, hazardous waste) have been selected assuming PET data available from experience and literature review.

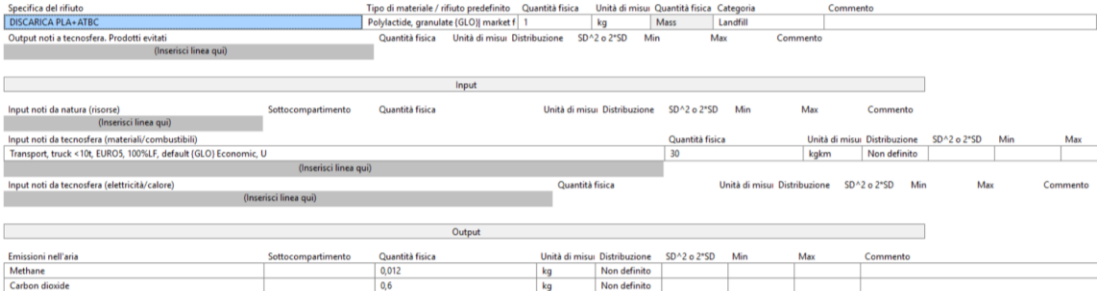
Recycling: in addition to the transport from the consumer to the collection centre, recycling usually includes also the transport from the collection to the sorting centre. In fact, plastic is generally sorted before sending to the recycling plant. The three electricity consumptions have been summed up in one. Regarding the freight, the previous assumptions have been made and same data have been selected, but changing the distance between the reference plant and the recycling plant. EPDM recycling data were assumed to be similar to PET (50). In recycling, the "known outputs to technosphere avoided products" consists of the resulting material obtained at the end of the process, in this case the synthetic plastic rubber. Furthermore, for the recycling process the yield has been assumed to be 15%, in light of the elastomer peculiarities.

PLA/ATBC disposal assumptions:

Regarding landfill, incineration and recycling of PLA/ATBC o-rings, disposal scenarios have been assumed similar to EPDM data, but considering half the values on the basis of similar studied approaches (50). Unit functional was always be assumed equal to 1 kg.

Landfill: half of the EPDM air emissions were considered in terms of carbon dioxide and methane, as shown in Figure 59.

Incineration: a plant efficiency of 75% was considered together with the calorific value of PLA assumed equal to 20 MJ/kg.



Specifica del rifiuto	Tipo di materiale / rifiuto predefinito	Quantità fisica	Unità di misur	Quantità fisica	Categoria	Commento
DISCARICA PLA+ATBC	Polylactide, granulate {GLO}| market f	1	kg	Mass	Landfill	

Output noti a tecnosfera. Prodotti evitati	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)							

Input

Input noti da natura (risorse)	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								

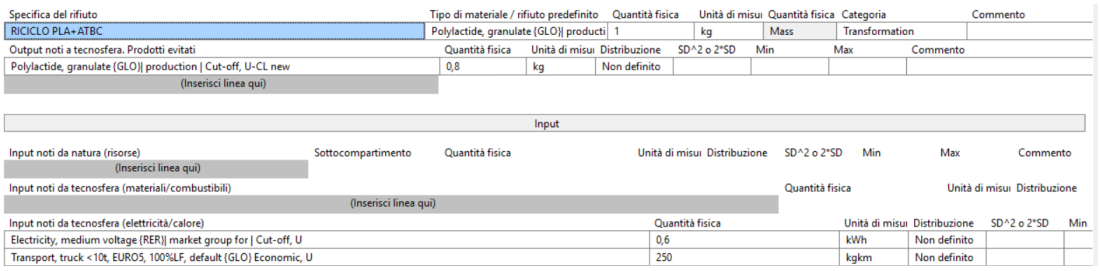
Input noti da tecnosfera (materiali/combustibili)	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max
Transport, truck <10t, EURO5, 100%LF, default {GLO} Economic, U	30	kgkm	Non definito			
(Inserisci linea qui)						

Input noti da tecnosfera (elettricità/calore)	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)							

Output

Emissioni nell'aria	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
Methane		0,012	kg	Non definito				
Carbon dioxide		0,6	kg	Non definito				

Figure 59 Landfill disposal for 1 kg of PLA/ATBC



Specifica del rifiuto	Tipo di materiale / rifiuto predefinito	Quantità fisica	Unità di misur	Quantità fisica	Categoria	Commento
RICICLO PLA+ATBC	Polylactide, granulate {GLO}| producti	1	kg	Mass	Transformation	

Output noti a tecnosfera. Prodotti evitati	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
Polylactide, granulate {GLO}| production | Cut-off, U-CL new	0,8	kg	Non definito				
(Inserisci linea qui)							

Input

Input noti da natura (risorse)	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								

Input noti da tecnosfera (materiali/combustibili)	Quantità fisica	Unità di misur	Distribuzione
(Inserisci linea qui)			

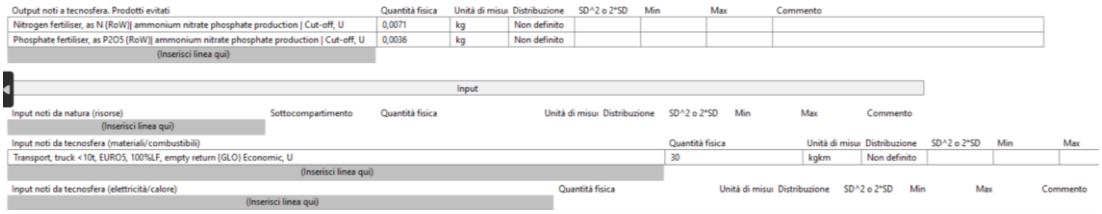
Input noti da tecnosfera (elettricità/calore)	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min
Electricity, medium voltage {RER}| market group for | Cut-off, U	0,6	kWh	Non definito		
Transport, truck <10t, EURO5, 100%LF, default {GLO} Economic, U	250	kgkm	Non definito		

Figure 60 PLA/ATBC Recycling

Recycling: the output of the process (avoided product) consisted in PLA granules with a yield of 80% as shown in Figure 60.

Composting: data have been taken from SimaPro database, adding Nitrogen and phosphate fertilisers among the avoided products as per literature studies on PLA composting (Figure 61).

Transport input in SimaPro was set by road, assuming the same truck used in the previous paragraphs. As described above, the distance assumed between the reference production plant and the composting plant was about 30 km.



Output noti a tecnosfera. Prodotti evitati	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
Nitrogen fertiliser, as N {RoW}| ammonium nitrate phosphate production | Cut-off, U	0,0071	kg	Non definito				
Phosphate fertiliser, as P2O5 {RoW}| ammonium nitrate phosphate production | Cut-off, U	0,0036	kg	Non definito				
(Inserisci linea qui)							

Input

Input noti da natura (risorse)	Sottocompartimento	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)								

Input noti da tecnosfera (materiali/combustibili)	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max
Transport, truck <10t, EURO5, 100%LF, empty return {GLO} Economic, U	30	kgkm	Non definito			
(Inserisci linea qui)						

Input noti da tecnosfera (elettricità/calore)	Quantità fisica	Unità di misur	Distribuzione	SD^2 o 2*SD	Min	Max	Commento
(Inserisci linea qui)							

Figure 61 Composting scenario

8.3 Life Cycle Impact Assessment

Characterization

After the flow chart and the system boundaries representation, together with the inventory definition, a quantitative approach follows the qualitative analysis previously conducted. In this regard, every substance contributes differently to the environmental impact. Each impact category is therefore characterised by a reference unit of measurement as well as characterization factors. These factors are used to quantify the incidence of a substance to a specific environmental impact. In this respect, the selection of the impact categories depends on the goal and scope of the analysis. In short, the main impact categories may include global warming, stratospheric ozone depletion, acidification, eutrophication, land use change, consumption of non-renewable resources.

Focusing on the environmental impacts' calculation, there are several methods including specific indicators. The indicators can be classified into midpoint and endpoint. Midpoint indicators provide results related to emissions into the environment without quantifying the damage; while endpoint indicators evaluate the phenomenon effects on both environment and man.

In essence, the impact categories employed for a LCA analysis are function of the calculation method adopted.

Method

Among the different methods, ReCiPe 2016 was chosen for the LCA evaluation. The complete name of the method was ReCiPe 2016 Midpoint (E) V1.07/World (2010) E/A, in which the egalitarian perspective was approached.

The method derives from ReCiPe 2008 which was first developed through cooperation between RIVM, Radboud University Nijmegen, Leiden University and PRé Sustainability (40).

One of the main goals of ReCiPe method is to shorten the long list of cycle inventory results, transforming it in a limited amount of data: indicator scores which express how severe the environmental impact is. In this sense, as reported by Bałdowska-Witos P. et al. (55), ReCiPe method provides factors based on different cultural perspectives, depending on time as well as technological development. Specifically, ReCiPe methods can be classified according to three cultural perspectives which feature different approaches, as described in the following list:

- Individualist: is a short-term method with a positive expectation that technology can avoid many problems in future;
- Hierarchist: is a consensus model and might be considered to be as a default model;
- Egalitarian: is a long-term model based on precautionary principle thinking.

The ReCiPe 2016 approach used in the PhD thesis provides Midpoint indicators and an Egalitarian perspective.

In light of the above considerations, the impact categories to be analysed are related to the calculation method ReCiPe 2016. They are eighteen and are synthetically shown in Table 25. In this regard, the ReCiPe 2016 method determines calculations according to eighteen indexes of the middle point and three indexes of the final points (55). Focusing on the final points, they can be classified according to three main sections such as human health, ecosystem quality and climate changes. Thanks to their reduced number, final points make the LCA results interpretation easier. To perform endpoint indicators evaluation, Endpoint (E) method has been adopted. The complete name of the method was ReCiPe 2016 Endpoint (E) V1.07/World (2010) E/A, in which the egalitarian perspective was approached.

The three endpoints analysed in the PhD thesis are summarized in the following list:

- Human health,
- Ecosystems,
- Resources.

Impact category	Unit of measurement
Global warming	kg CO_2 eq
Stratospheric ozone depletion	kg CFC_{11} eq
Ionizing radiation	kBq Co-60 eq
Ozone formation, Human health	kg NO_x eq
Fine particulate matter formation	kg PM2.5 eq
Ozone formation, Terrestrial ecosystems	kg NO_x eq
Terrestrial acidification	kg SO_2 eq
Freshwater eutrophication	kg P eq
Marine eutrophication	kg N eq
Terrestrial ecotoxicity	kg 1,4-DCB
Freshwater ecotoxicity	kg 1,4-DCB
Marine ecotoxicity	kg 1,4-DCB
Human carcinogenic toxicity	kg 1,4-DCB
Human non-carcinogenic toxicity	kg 1,4-DCB
Land use	m2a crop eq
Mineral resource scarcity	kg Cu eq
Fossil resource scarcity	kg oil eq
Water consumption	m_3

Table 25 Impact categories for ReCiPe 2016 method -Midpoint

As described by Manfredi M. (49), inventory data are transformed into the potential impact named EP(j)i by multiplying the various substances, named Qi, with their characterization factors, named EQ(j)I, as expressed by the following formula:

$EP(j)i = Qi * EQ(j)i$

The overall impact may be then calculated by the sum of the single impacts associated with the substances. Afterwards, a normalisation stage usually takes place.

In the normalisation phase, the values obtained during characterization are divided by a reference value so that the magnitude of each environmental effect can be established.

For the assessment of the environmental impact of each formulation, normalisation was done for each impact category by the maximum value between the different stages of the product life cycle. For the comparative LCIA of the two products, normalisation was done for each impact category for the maximum value between the two materials.

In light of these considerations, experimental data have been normalised and then processed by the software Origin 2018, since it is particularly efficient for customizing bar and column graphs.

Environmental impacts evaluation of EPDM and PLA/ATBC o-ring life cycle is shown respectively in Figure 62 and Figure 64. While the comparative Life Cycle Assessment of the two products' life cycle is illustrated in Figure 66. Concurrently, the final endpoints of ReCiPe 2016 method have been analysed as described in the previous paragraphs. Regarding EPDM and PLA/ATBC o-ring life cycle, normalization of impacts is indicated in Figure 63 and Figure 65, whereas the comparison between EPDM and PLA/ATBC impacts in Figure 67. As shown, the end-of-life impact of the EPDM o-ring is higher than the other life cycle steps of the same material as well as the PLA/ATBC o-ring and results extremely harmful to human health.

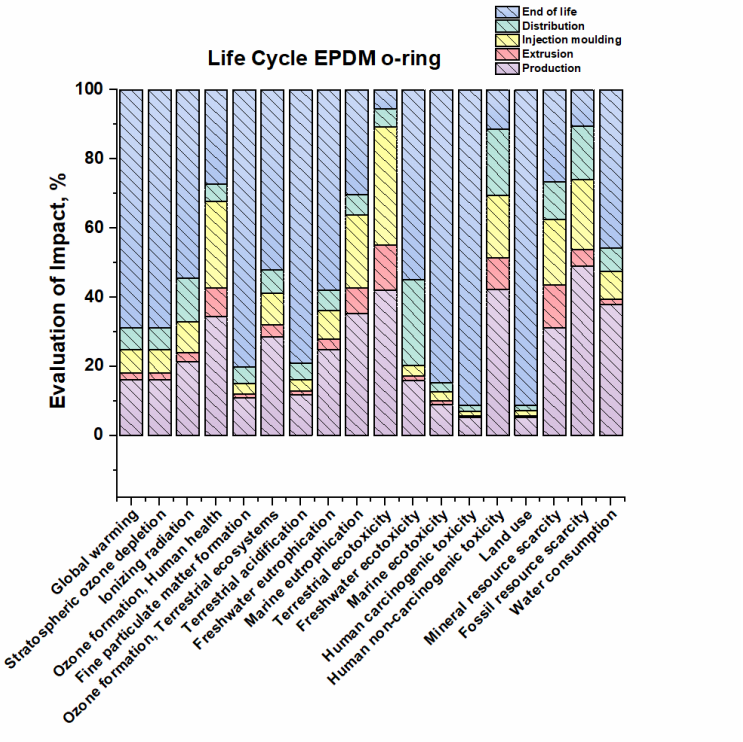


Figure 62 Characterization of EPDM o-ring impacts

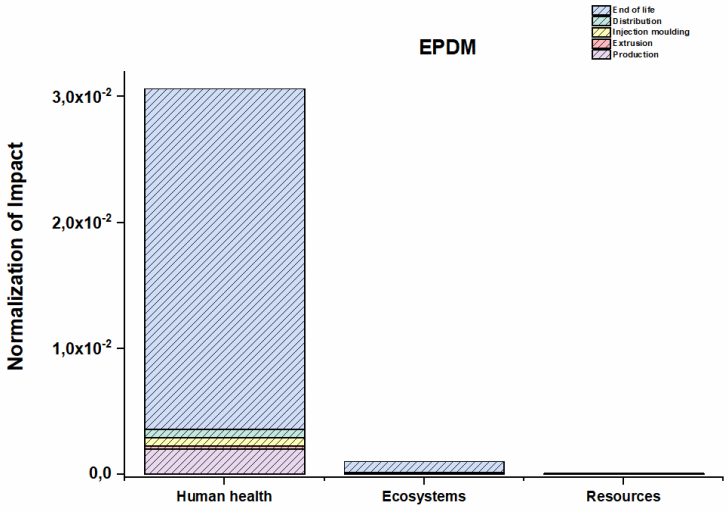


Figure 63 Normalization of EPDM o-ring impacts

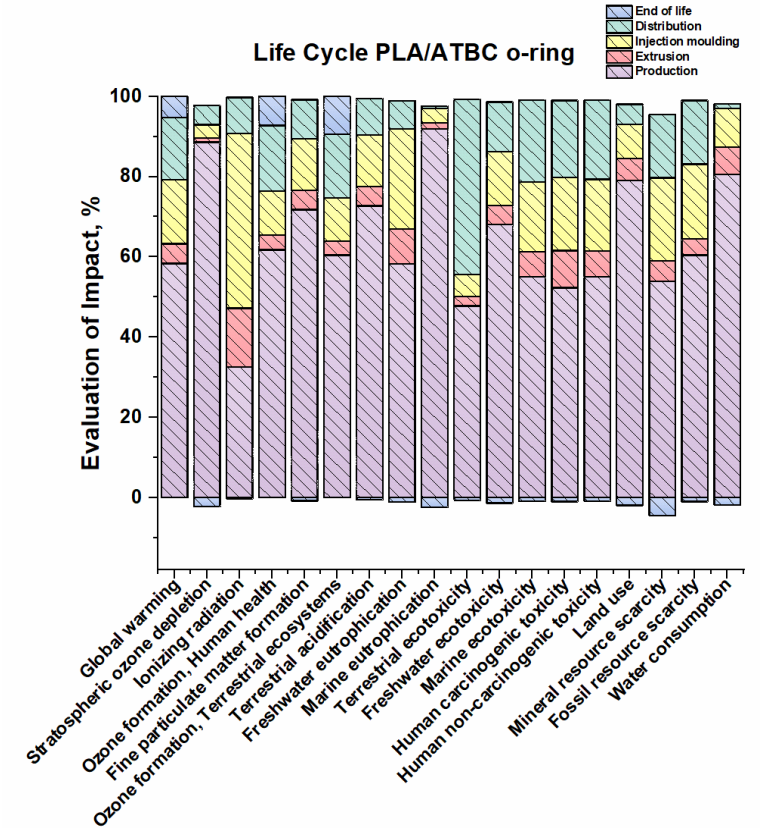


Figure 64 Characterization of PLA/ATBC o-ring impacts

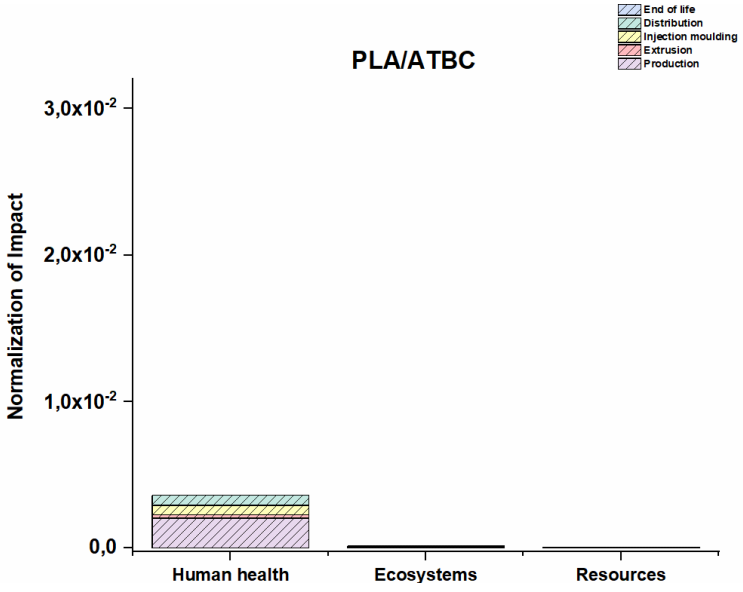


Figure 65 Normalization of PLA/ATBC o-ring impacts

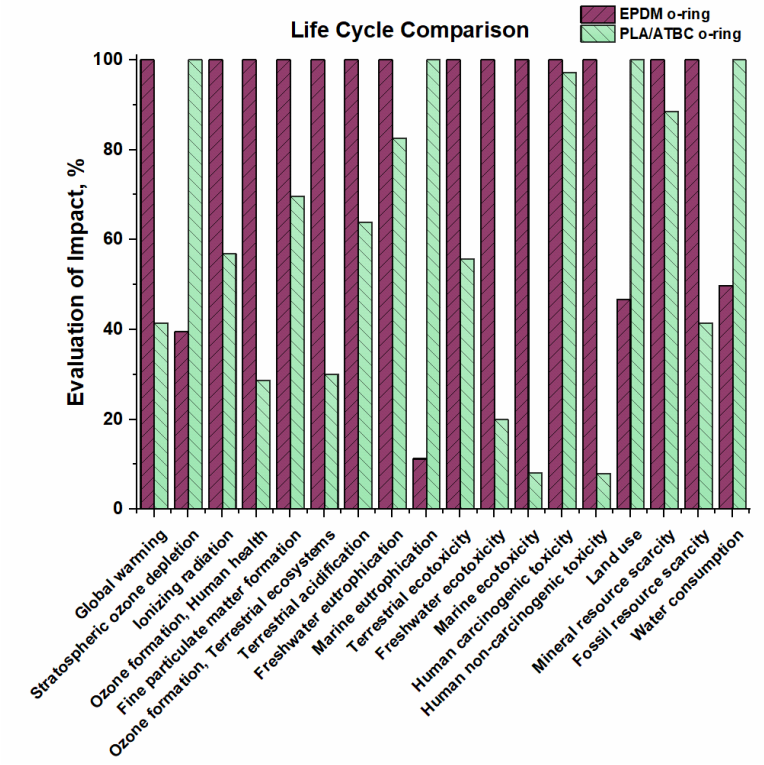


Figure 66 Life cycle comparison impact assessment

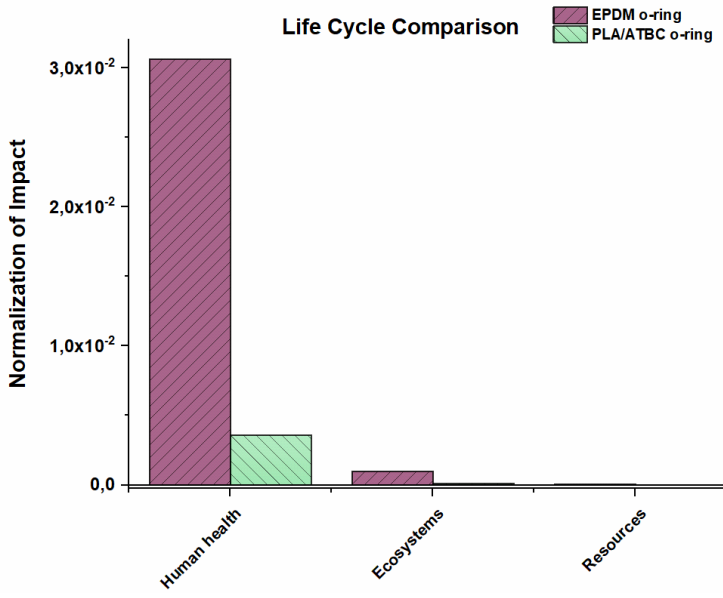


Figure 67 Comparison between EPDM and PLA/ATBC o-rings impacts

8.4 Life Cycle Interpretation

Following the analysis of the LCA results and graphs, it is worth underlining that the ReCiPe 2016 Egalitarian method can be considered a conservative approach, since it represents a long-term model based on precautionary principle thinking, as described in the previous sections.

Focusing on the LCIA of **EPDM** o-ring, the disposal phase, or end-of-life, is the stage that weighs heavily on the entire life cycle in most of the impact categories. This depends on the incineration rate assumed equal to 88%, on a very low recycling rate according to literature (2%), and an assumed landfill rate of 10%. Furthermore, production stage shows a significant impact, especially in the global warming, stratospheric ozone depletion and formation categories, as well as land use, mineral resource scarcity, fossil resource scarcity and water consumption. These phenomena are due to the consumption of fossil sources for the production of the raw materials. Same applies for the categories of freshwater and marine eutrophication, in which the production stage shows higher impact than the other stages. Nevertheless, for those categories, injection moulding shows also a considerable environmental impact.

Focusing on Global warming factor, it is generally calculated by considering, among the several substances emitted in air, those that contribute to the potential global warming of the planet. They are methane (CH_4), carbon dioxide (CO_2), nitrogen dioxide (NO_2), chlorofluorocarbons (CFCs) and further halogenated organic compounds that constitute greenhouse gases (GHGs). Whereas the Ozone depletion represents the degradation level of the ozone layer that can be generated by a substance. In this regard, the so-called Ozone Depleting Substances (ODS) are capable of destroying ozone molecules by transforming them into oxygen; thus, thinning the stratospheric ozone layer and letting UV rays pass through it.

Regarding the evaluation of **PLA/ATBC** o-ring life cycle impacts, the end-of-life stage shows very low environmental impact compared to the other life cycle phases, as expected. The end-of-life is barely noticeable in the graph and this is due to the high rate of composting, set equal to 57%.

Focusing on the production stage, it seems, instead, to show higher environmental impact in most of the categories compared to the other life cycle stages. However, injection moulding stage also reveals a noticeable environmental impact in most categories.

In this regard, it is worth underlining that on the basis of the experience and the scientific literature, PLA production by SimaPro modelling significantly affects LCA results. Hence, the inventory provided by the libraries influences the production emissions, making the production stage particularly impactful compared to the others life cycle stages. Specifically, PLA manufacturing impact evaluation includes fermentation and polymerization of lactic acid, energy consumption, as well as waste generation and emissions (46).
In light of the above considerations, further calculation has been conducted to evaluate the influence and weight of PLA production stage.
Tests have shown that changing both input and output parameters, particularly reducing them to only one geographical data set in SimaPro, leads to a drastic reduction in global warming category, in fossil resource scarcity and mineral resource scarcity as well as in freshwater and marine ecotoxicity.

Finally, focusing on the **comparative LCIA** of the two products, despite the use of an impactful PLA modelled by SimaPro database as described before, the life cycle of a traditional plastic o-ring made of EPDM shows environmental impacts in many of the categories higher than the prototype bio-elastomer made of PLA/ATBC. These phenomena are due to the fossil sources from which raw materials are extracted via related energy-intensive processes. Moreover, the end-of-life of traditional plastic o-ring like EPDM is more impactful. One of the issues to consider is the water that may seep through plastic waste generating a liquid called leachate, which then transports pollutants into the soil. In addition, traditional plastic disposal leads to a higher rate of pollutant air emissions, like CO_2 and methane. On the other hand, the bio-elastomer PLA/ATBC life cycle shows higher environmental impact than EPDM among the specific categories related to PLA production.

PLA is actually obtained by maize grain production which involves both land use and water consumption for irrigation. In addition, the use of fertilizers and pesticides may lead to potential alteration on soil quality as well as intensive agriculture (46). Concurrently, the raw materials extraction such as maize, sugarcane, corn starch are energy demanding, and require irrigation.

Furthermore, eutrophication impacts are mainly related to lactic acid production since the release of nitrogen into water and air occurs, according to Musienko, I (46). On this point, Morao A. and de Bie F. specifically describe aquatic eutrophication as nutrient enrichment of the aquatic environment (47). Marine eutrophication regards the nitrogen enrichment of seawater, while freshwater eutrophication only phosphor enrichment of freshwater. Instead, terrestrial eutrophication is due to the deposition of aerial nitrogen compounds such as No_x and NH_3.
Besides the above, PLA production, as defined in SimaPro modelling, involves various chemical waste emissions in the production phase, leading to severe impact among toxicity categories.

8.4.1 Sensitivity analysis

Further LCIA analyses have been conducted by ranging the split between the different disposal methods. The sensitivity analysis on end-of-life scenario is synthetized in Table 26. For EPDM, the recycling content has been increased to 75% assuming for rubbers and elastomers the CONAI data on the plastic recycling amount reached in Italy in 2023: it was equal to 75,3% (45). Specifically, CONAI or Consorzio Nazionale Imballaggi (National Packaging Consortium) is an Italian private consortium that operates on a non-profit basis, it embraces the response of private companies to the environmental problem, in compliance with guidelines and objectives set by the political system. It is worth underlining that 75% is nowadays a theoretical and extremely high value for elastomers recycling, but it aims to change the point of view of the analysis.

For PLA/ATBC, an inversion of the recycling and landfill split was carried out in order to perform the sensitivity analysis. Incineration rate has been arbitrarily assumed equal to 15%. While composting ratio has been left unaltered.

Disposal scenario	EPDM	PLA/ATBC
Recycling	75%	25%
Incineration	15%	15%
Landfill	10%	3%
Composting	-	57%

Table 26 Sensitivity analysis on disposal scenario

Sensitivity analysis on end-of-life scenario of EPDM and PLA/ATBC o-ring is shown respectively in Figure 68 and Figure 70. Focusing on EPDM graph, results show that increasing the recycling rate of elastomers to the theoretical value of 75% would greatly reduce the environmental impact of fossil plastic in many impact categories, especially in global warming and ecotoxicity fields. While PLA/ATBC sensitivity analysis illustrates that the change in the disposal scenario passing from 3% to 25% of recycling leads to negative end-of-life impacts compared to the other life cycle stages: this phenomenon is due to the increased percentage of avoided products. These results stress the importance of adopting recycling method instead of landfill. However, PLA production remains the highest impactful stage: as previously described, it strictly depends on SimaPro modelling.

The comparative LCIA of the two analysed products life cycle according to the sensitivity study is illustrated in Figure 72. The graph shows that increasing the recycling rate of plastics to theoretical value equal to 75% leads to lower environmental impacts among many categories, especially in stratospheric ozone depletion and ozone formation. The study shows that investing in future recycling technologies for traditional plastics and particularly for rubber and elastomer sector is as good strategy as for bioplastics and would allow to use the already established technologies, not disrupting processes.

On the other hand, increasing the recycling rate of PLA/ATBC is a more energy-intensive process, leading to a slight raise in some impact categories.

Focusing on endpoint indicators, normalization of impacts of EPDM and PLA/ATBC o-ring life cycle is shown in Figure 69 and Figure 71, whereas the comparison between EPDM and PLA/ATBC impacts in Figure 73.

Overall, environmental impacts on human health decrease, especially for EPDM, based on the sensitivity analysis hypothesis and particularly on the increased recycling split of the end-of-life scenario.

It is worth underlining that polymer waste presents high variability in the composition, making recycling complicated and leading to less effective final properties of the recycled materials (61).

Regarding the sensitivity analysis, the adoption of a 75% recycling rate for EPDM, although theoretical, shows a significant reduction in environmental impact.

EPDM is typically vulcanized with sulphur or with peroxides (66), therefore it reveals a chemically cross-linked structure which makes its recycling demanding (65).

Rubber recycling can be generally performed via three methods (65) that can be listed as: 1) fragmentation, 2) pyrolysis, 3) devulcanization.

With regard to the first approach, EPDM can be recycled to produce TPEs via melt blending of small particles with thermoplastics. However, compatibility between rubbers and thermoplastics appears low and so does the interfacial adhesion, leading to low mechanical properties, especially elongation at break; furthermore, this effect becomes more noticeable at higher rubber concentration, above 50 wt% (61). Alternatively, EPDM particles can be used as fillers within virgin EPDM compounds (65).

In addition, Anand A. et al. (64) studied the mechanical shredding of EPDM waste rubber and its blending with virgin rubber compounds selecting two proportions: 30 and 40 wt%. The research shows that the recycled materials might be used in soft flooring applications, turning into a cost-saving and sustainable alternative to traditional choices.

The second method is pyrolysis, which converts different polymers waste by thermal energy into monomers or pyrolysis oil; it especially suits for mixed heterogeneous flow, since it does not involve preliminary waste split (65).

Devulcanization is the third recycling method: as described by Pirityi D. et al. (67), the process allows to transform rubber waste into its primary uncured structure through the scission of covalent crosslinks within the rubber matrix. In fact, devulcanization allows revulcanization of devulcanized samples in order to obtain a new vulcanized compound with both virgin and devulcanized material and is particularly efficient when rubber waste stream is homogenous. In this perspective, theoretically EPDM waste could be easily processed as homogeneous, due to its specific fields of application (65).

Among the wide range of devulcanization methods that can be approached, Pirityi D. and Pölöskei K. (66) studied thermomechanical devulcanization of sulphur-cured EPDM rubber. The devulcanized material was then recycled via revulcanization, adding extra curing agents. Finally, a series of blending tests with virgin EPDM was performed with 25, 50, 75, 100 wt% of recycled content. The second research phase involved characterization tests on the blends, with focus on mechanical properties. It was found that elasticity was compromised at 75 and 100 wt% devulcanized content; on the other hand, a decrease in tensile strength was observed by 15% and 20% for blends with respectively 25% and 50% recycled content.

Most literature studies reveal that large-scale EPDM recycling methods are still in progress, hence more research should be carried out and implemented in the near future to find the proper recycled percentage to be used. Overall, up to 50 wt% of recycled EPDM content might be approached according to the different recycling strategies. Recycling EPDM might support Circular Economy and reduce environmental impacts related to virgin synthetic rubber production.

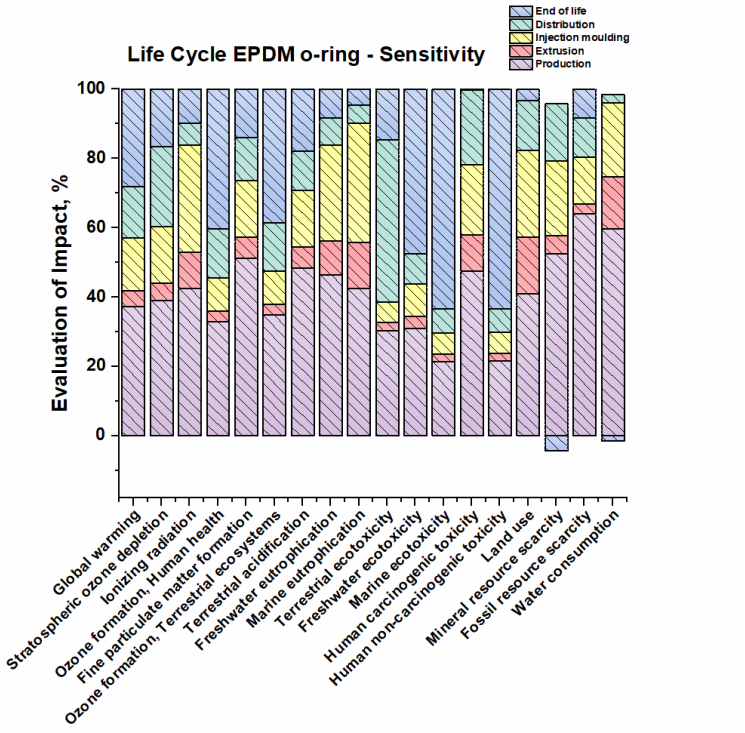


Figure 68 Characterization of EPDM o-ring impacts -Sensitivity

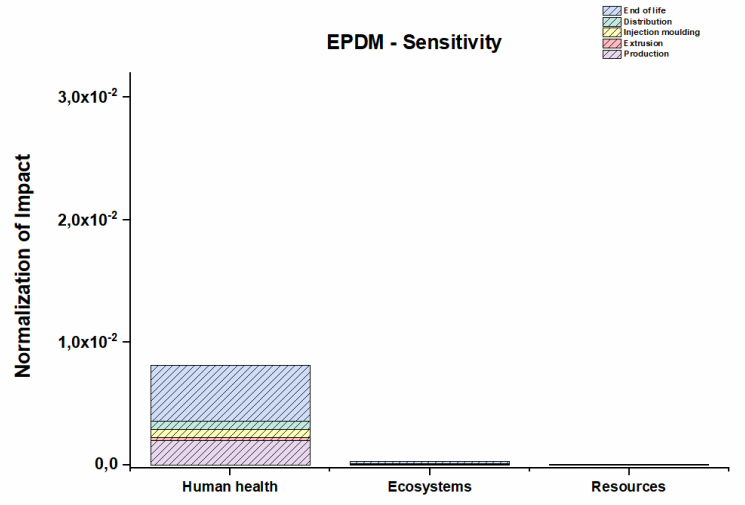


Figure 69 Normalization of EPDM o-ring impacts-Sensitivity

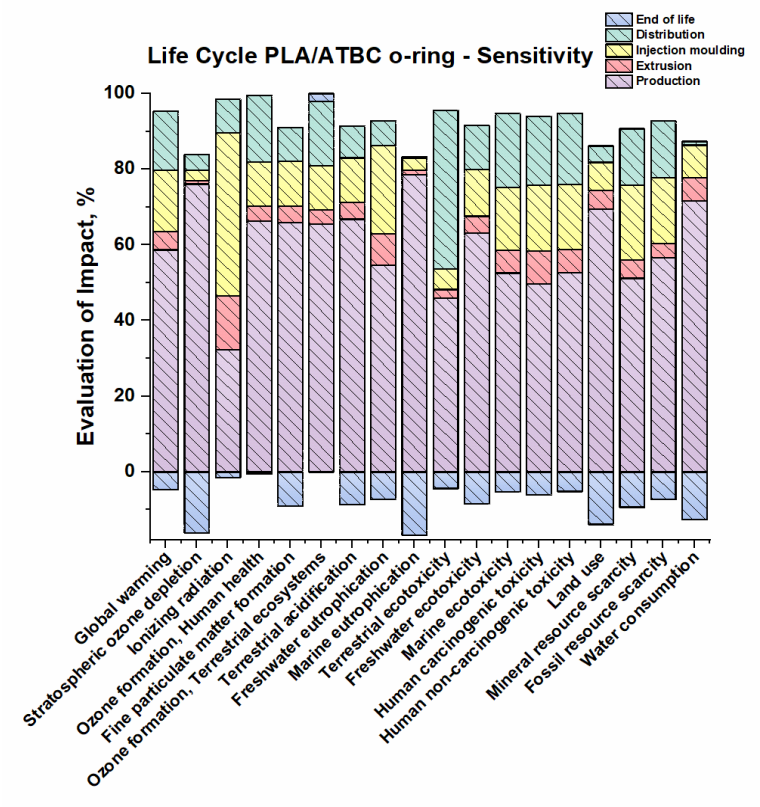


Figure 70 Characterization of PLA/ATBC o-ring impacts -Sensitivity

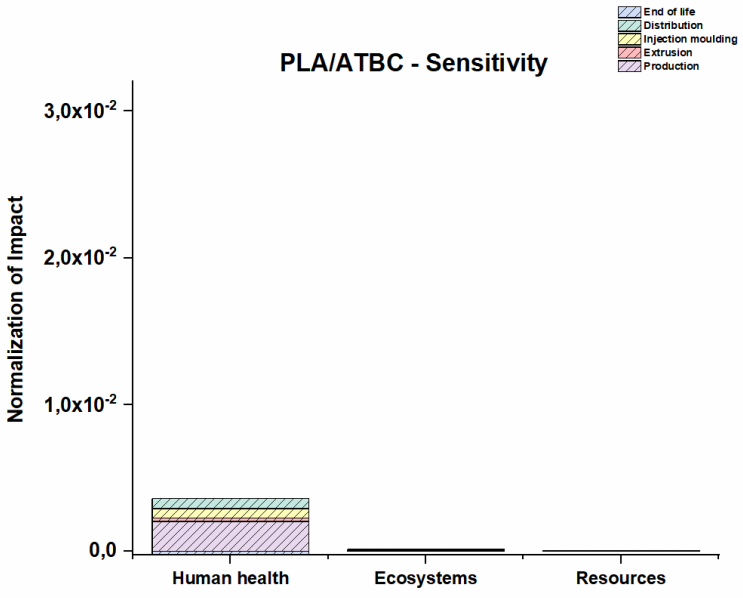


Figure 71 Normalization of PLA/ATBC o-ring impacts-Sensitivity

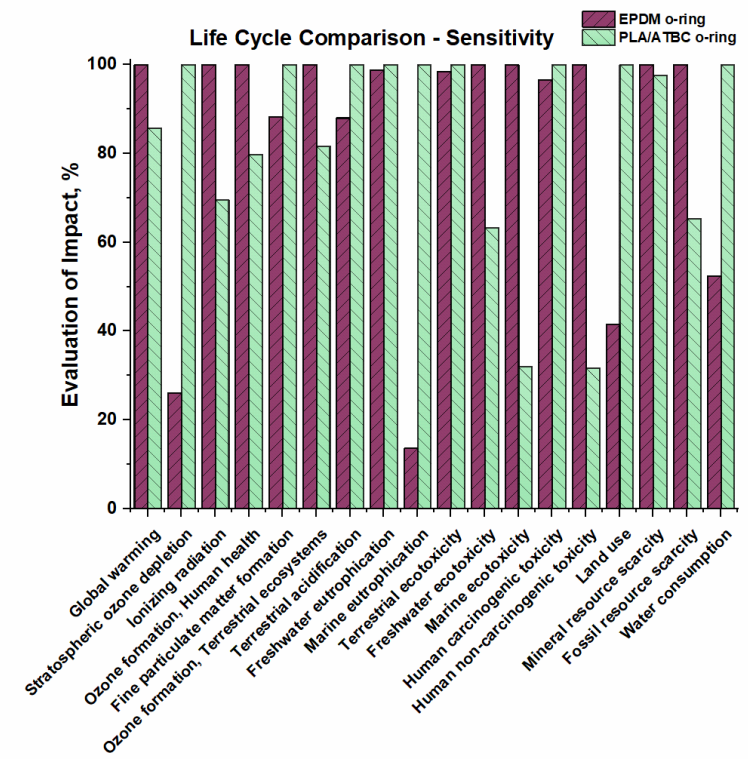


Figure 72 Life cycle comparison impact assessment-Sensitivity

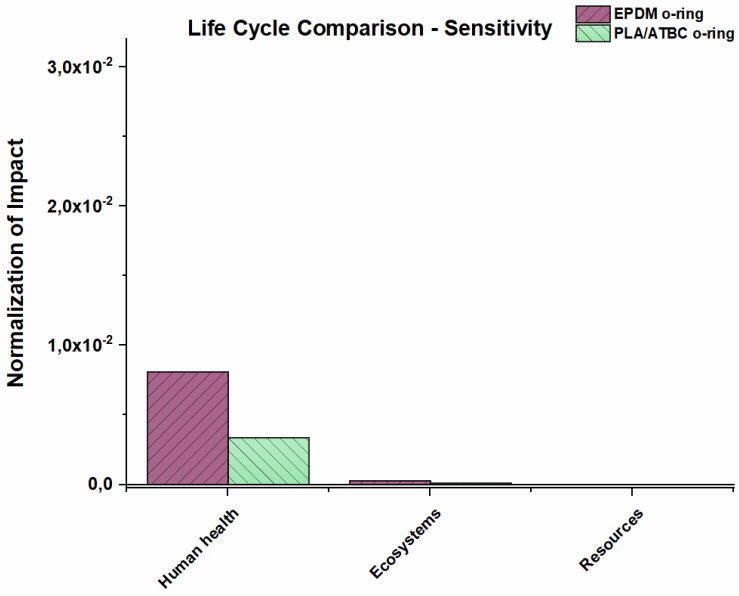


Figure 73 Comparison between EPDM and PLA/ATBC o-rings impacts-Sensitivity

9. Conclusion and future developments

The purpose of the PhD thesis is to design and develop a biodegradable and compostable elastomer with a high degree of innovation, technological content and a low environmental impact. The research has been restricted to the industrial field of automotive applications, focusing on conventional elastomers generally produced from fossil sources.

Nowadays, environmental plastic pollution is an issue of collective interest. In essence, the PhD research has been conducted with the aim of developing an eco-friendly elastomer in consistency with the policy *a greener, low-carbon transitioning towards a net zero carbon economy* of the React-EU plan.

During the three-years PhD, a scientific literature review has been conducted to study a wide range of biopolymers, additives and fillers in order to study and analyse their thermo-mechanical and rheological properties in comparison with traditional thermoplastic elastomers (TPEs). The study phase has always been followed by a practical research stage in laboratory.

Firstly, bio-based, biodegradable and compostable polymers have been selected for the definition of the prototype formulations: PLA or polylactic acid. Three blends have been studied based on a PLA matrix; the addition of a secondary biopolymeric phase and/or a liquid biodegradable plasticizer was also implemented. Furthermore, formulations were classified according to the different nature of PLA: on one hand a standard semi-crystalline and brittle grade; on the other a more challenging amorphous grade featuring grease barrier, useful to the final application. In essence, the use of Acetyl Tributyl Citrate (ATBC), P3HB4HB (PHACT) and the combination of them was assessed to improve the flexibility and the elongation of PLA. On this point, the three formulations have been respectively named: PLA/ATBC, PLA/PHACT, PLA/PHACT/ATBC.

Secondly, compounding was assessed to prototype the blends via a lab-scale twin screw extruder. Three compounds have been extruded in pellet form to later feed a lab-scale single screw cast extruder to produce prototype sheets.

Along with extrusion processes, thermal (DSC) and rheological (MFI, Rheometer) characterization tests were conducted to explore the properties of the experimental compounds, as well as tensile tests were performed on the sheets.
After the analysis of a wide range of laboratory tests conducted on the biopolymeric formulations together with the lab-scale extrusions (reactive and cast extrusion), PLA/ATBC blend has shown better performances both in terms of processability and elastic recovery, resulting in a prototype bio-elastomer. On the other hand, although PLA/PHACT/ATBC showed lower yielding and stress at break, it featured comparable elongation at break to PLA/ATBC and high biodegradation kinetic rate aided by PHACT addition. For this reason, the blend PLA/PHACT/ATBC might be further engineered with fillers and additive packages.

Finally, the Life Cycle Assessment (LCA) method has been adopted to assess the environmental impact of the prototype bio-elastomer PLA/ATBC compared to a traditional TPE named EPDM, using a *cradle-to-grave* approach. In this regard, LCA analysis allows to quantify the environmental impact of products and production systems, via the identification of materials production and energy requirement as well as the emissions releasing during the entire life cycle of the product. SimaPro software has been used to perform the environmental impacts calculation; specifically, ReCiPe 2016 method has been adopted with Midpoint indicators and an Egalitarian perspective. Considering the assumptions made during the analysis, LCA results have illustrated that the prototype blend PLA/ATBC shows lower environmental impacts during his life cycle in many impact categories when compared to the traditional plastic elastomer (EPDM) chosen for the study. Further sensitivity analyses have been conducted on end-of-life scenarios.

In light of the above considerations, future developments of this research may include further laboratory analyses to obtain a complete characterization of the prototype material with the aim to evaluate the concrete possibility of producing biodegradable and compostable o-rings. Further analyses and evaluations might be even conducted to determine whether the possibility of a scale-up, switching the research from laboratory to pilot-industrial scale.

Since the research topic might be extended to several industrial applications, additional studies might be implemented to continue the design and development of compostable and recyclable bio-TPEs.

Indeed, the versatile nature of the biopolymers and the additives used in the PLA/ATBC blend, together with the promising mechanical results obtained, might allow to extend the prototype bio-elastomer to future developments, e.g. in the medical and health-care sector. In fact, the selected biopolymers and additives used in the blend yields to a high transparent biodegradable and compostable elastomer, or briefly bio-elastomer.

Among the possible industrial applications that may suit the research and may be explored, there is the baby nappy sector. Thus, elastomers are usually used for the side closures of the diapers, since they allow to adjust the diaper without damaging it.

Due to the outstanding properties featuring the biodegradable materials employed in the prototype PLA/ATBC blend -which are even suitable for food contact applications- the promising bio-elastomer might potentially suit a wide range of industrial applications.

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PhD in
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Study, design & development of compostable and recyclable elastomers with a high degree of innovation, technological content and low environmental impact

PhD Student:
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XXXVII Cycle