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DEVELOPMENT AND CHARACTERIZATION OF BIOPOLYMERS

Tesi di laurea magistrale in BIOCARBURANTI e BIORAFFINERIE

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ABSTRACT

Development and characterization of biopolymers was done in AIJU's laboratories. AIJU, Technological Institute for children's products and leisure is based in Spain. The work has the aim to study qualities and characteristics of bioplastics' blends, in order to design where improvements can be executed. Biopolymers represent a sector with great development possibilities because they combine high technical potential and eco-sustainability. Nowadays, plastic pollution has becoming increasingly concerning, particularly in terms of management of waste. Bioplastics provide an alternative for the disposal of products, reducing the volume of waste and enhancing the end of life recovery. Despite the growing interest in biopolymers there is some gaps that need be filled. The main objective on this work, is the optimization of bioplastics mechanical properties, to find suitable substitutes, as similar as possible to conventional plastics. Firstly, investigations on processability of biomaterials has been deepen since the project deals with toy manufacturing's sector. Thus, starting from laboratory scale the work aspires to expand industrially. By working with traditional machines, it was notable that, with some limited modifications, the equipment can perform the same functions. Therefore, operational processes do not emerge as an obstacle to the production chain.

Secondly, after processing bio-blends, they are characterized by thermal tests (melt flow index, differential scanning calorimetry-DSC, thermogravimetry-TGA) and mechanical tests (traction and flexural tests, Charpy impact, SHORE D hardness and density). While the compatibility does not show relevant results, mechanical improvements has been visualized with addition of more ductile materials. The study was developed by inclusion of sustainable additive VINNEX® to blends. The thesis has highlighted that integration of more flexible materials provides elasticity without compromising bioplastics' properties.

Summary

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For designing chemical structures CHEMDRAW 19.1 was used.

SMILES structures were taken from website source PUBChem.

Glossary

PET- Polyethylene Terephthalate

HDPE- High-Density Polyethylene

PVC- Polyvinyl Chloride

LDPE- Low-Density Polyethylene

PP- Polypropylene

PS- Polystyrene

BPA- Bisphenol A

CO_2- Carbon dioxide

O_2- Oxigen

H_2O- Water

PCCPs- Personal care products and cosmetic products

HABs- Harmful algal blooms

P- Phosphorus

Ni- Nitrogen

C- Carbon

Mg- Magnesium

K- Potassium

EDCs- Endocrine disruptors chemicals

PAHs- Polycyclic Aromatic Hydrocarbons

PCBs- Polychlorinated biphenils

GHG- Greenhouse gases emissions

PLA-Polylactic acid

TPS- Starch and thermoplastic

PHAs- Polyhydroxyalkanoates

PBS-Polybutylene succinate

PCL-Polycaprolactone

ISO- International Organization for Standardization

DSC- Different scanning calorimetry

TGA- Thermogravimetry

FTIR-Fourier-Transform infrared spectroscopy

MFI-Flow index determination

Tm- Melting temperature

Tg- Glass transition temperature

Et- Tensile modulus, Young’s modulus

σb- Tensile strength at break

Ɛb- Deformation value, elongation at break (%)

INTRODUCTION

Plastics is the commonly term used to describe a wide range of synthetic or semi-synthetic materials. Since plastics introduction, approximately 100 years ago, the proliferation so readily throughout the modern world is due to their versatility. Now, plastics is the most used material. Thanks to its qualities, it has helped society to simplify, make safer and enjoyable our daily lives. Plastic is relatively cheap, durable and can even help reduce energy consumption in many circumstances. However, plastic is a polarising material because of the stark benefits and drawbacks it presents, and the multiple ways it can impact human health, environment, and economy. Since plastic is ubiquitous material its overabundant uses are becoming a threat for humans and environment. Too often the ways plastics are currently produced, used and discarded fails to capture the economic benefits.

In the last years, the million tonnes of plastic litter that end up in ocean and landfill are the most visible and alarming signs, which are causing growing public concern. Plastic covers great contribution to climate change by greenhouse gas emissions. This is a largely hidden and invisible dimension of plastic, that is still poorly understood. The climate crisis remains not too much considered, creating significant uncertainties that threaten global efforts to avoid the most catastrophic impacts of climate change.

With the Paris Climate Agreement in 2015, the world committed to work together for limiting global temperature rising to well below 2°C and more. To achieve this goal society’s efforts must focus on strategies that aim to transform rapidly energy and transportation systems (which account 39% of annual global greenhouse gas emissions).

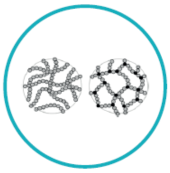
Solving plastic problems whilst maintaining the benefits of plastic is something that needs to be investigated. Redesigned products, developing new plastic strategy, using more suitable alternatives materials and substitutes where is beneficial are ways that need to be deepen. Furthermore, reducing plastic use and waste rates, re-using, re-purposing, and recycling plastic where possible, upgrading and maximizing plastic waste management systems, technology and facilities, are all potential and powerful starting points actions. However, rethinking and improving the functioning of a complex value chain requires efforts and cooperation by all its key players, from plastics producers to recyclers, retailers, and consumers.

Each one, as individuals, can help by making lifestyle changes, starting from recycling more at home and outside. Contribution is small but together, collective action is powerful.

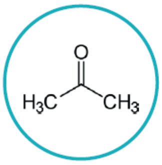
1. PLASTIC

IUPAC (International Union of Pure and Applied Chemistry) defines plastics materials as “polymeric materials which may contain substances aimed at improving their properties or reducing their costs"[1].

Plastic is a synthetic organic polymer.



Polymer



Organic

Synthetic

Plastic is not a single material, but family of materials with different properties. Thanks to versatility of plastic, innovation and market always try to meet consumer’s needs by offering a wide range of different plastics materials. Each one is designed with specific characteristics that make it ideal for the application to which it is intended providing the most efficient solution.

Currently, two major categories are presented in the plastic’s market: thermosets and thermoplastics. All the production processes of plastics involve using heat and/or pressure to form plastic useful products.

1.1. Polymers

Polymer is a molecule of high relative molecular mass and are composed of a large number repeating units of identical structure which are known as monomers[1]. Usually, polymers have high melting and boiling points and, depending on the length of the chain, high molecular masses. Carbon is the most important element in polymers. Carbon starts with four valence electrons and shares four more, forming a wide variety of covalent bonds (one pair of shared electrons). Long, strong chains of nets are made of thousands of carbon atoms form the backbone of a polymer.

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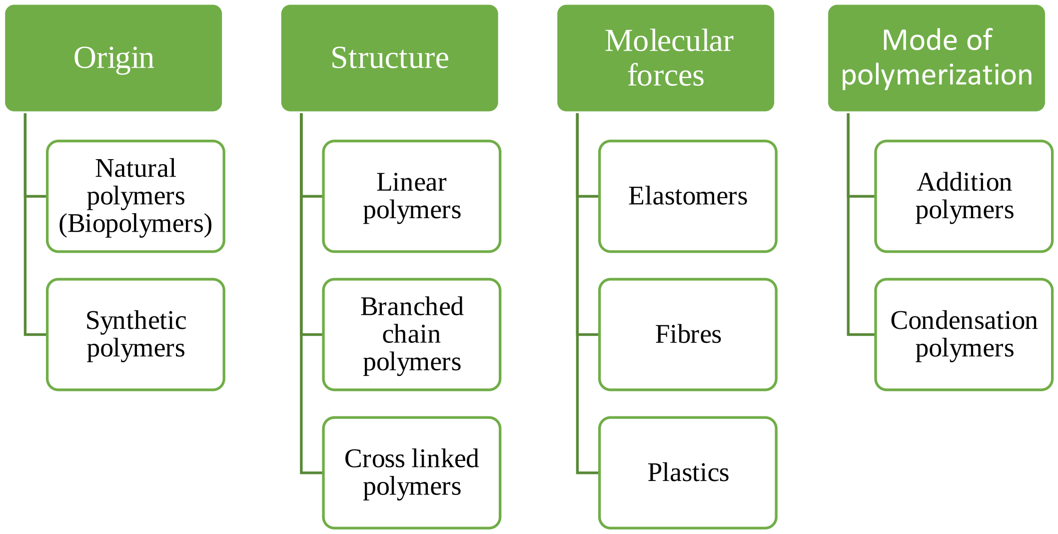
[1] **Monomer:** is a repetitive unit characteristic of polymer itself. The monomer can form covalent bonds with a sequence of additional like or unlike molecules under the conditions of the relevant polymer-forming reaction used for a specific process. [35]

Diagram 1- Classification of polymeric materials



1.1.1. Origin

Plastic materials can be produced from different sources. Its raw material can be of fossil origin (crude oil, gas, etc) or renewable (sugar cane, starch, vegetable oils, etc). In the same way, polymers may be divided into two categories: natural and synthetic.

- *Natural polymers* are presented in nature (animals and plants) and produced in the growth cycles of cells of living organisms. They include cellulose, oils, starches but carbohydrates, proteins, DNA and RNA and fats as well.
- *Synthetic polymers* are prepared by a chemical reaction, often in a lab. This category is wider, more consistent, and stable than natural polymers. Unfortunately, the stability of synthetic polymers makes that they do not break down in the natural environment.

1.1.2. Structure and molecular forces

There are three basic polymer structures according to concatenation and dislocation of the repeating units in the macromolecules: linear, branched, cross-linked polymers.

- *Linear polymer*: the macromolecules are developed in one preferential direction. The long chains are held together by the weaker Van der Waals or hydrogen bonding. These bonding types are relatively easy to break with heat. Thermoplastic are typically linear polymers.

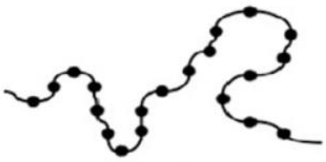


Figure 1.1- Linear polymer chain

- *Branched polymer*: the macromolecules are developed in more directions and thanks to distribution are less dense than linear polymers. Since the short chains do not link one longer backbone to another, heat may break the bonds between the branched polymer chains. Branched polymers could develop in thermoplastics.

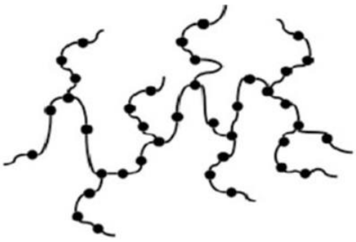


Figure 1.2- Branched polymer chain

- *Crosslinked polymer*: macromolecules are linearly anchored to each other by intermolecular transverse bonds, forming a compact, insoluble, infusible three-dimensional reticule.

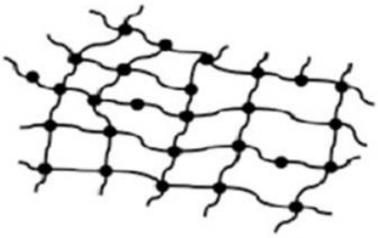


Figure 1.3- Crosslinked polymer chain

1.1.3. Molecular forces

Based on molecular forces, polymers can be classified on how the atoms in the molecules (macro or small) are linked together, in other words on the type of bond. The type of bond depends on the electronic configuration of atoms. The chemical bonds can be primary (strong bond) or secondary (weak bond).

- *Elastomers*: linear polymers that demonstrate the property of elastic deformation. When force is applied the material is stretched, but when the force is removed the material returns to its original configuration (shape and size). This behaviour is due to the presence of weak intermolecular forces (hydrogen, polar groups, and Van der Waals).
- *Fibres*: are made up of long and linear polymer chains that lie in the same direction of fibre itself (parallel). A peculiar feature is the resistance to extension and stretching in fibre's directions since the chains are already aligned.
- *Plastics*: are polymers with high molecular weight. They fall between the structural extremes represented by fibres and elastomers. At room temperature are hard and rigid, however they may be reshaped by heating according to their structures.

1.1.4. Mode of Polymerization

Polymerization[2] is a process in which monomers combine chemically to produce a larger chainlike or network molecule, called polymer. Two classes of polymerization are distinguished.

- *Condensation Polymers*: the polymer chain is obtained by condensing units resulting in loss of small molecules, such as water and alcohols.
- *Additional Polymers*: the structural units coincide with the starting monomer. The molecular weight of total polymer is the sum of molecular weights of monomers present in the chain.

Plastics are made from natural, organic materials such as cellulose, coal, natural gas and, of course, crude oil. Crude oil is a complex mixture of thousands of compounds and needs to be processed before it can be used. The production of plastics begins with the distillation of crude oil in oil refinery. The heavy crude oil is split into groups of lighter components, called fractions. Each fraction is a mixture of hydrocarbon chains (chemical compounds made up of carbon and hydrogen), which differ them in terms of size and structure of molecules. One of these fractions, called naphtha, is the crucial compound to produce plastics.

1.1.5. Thermal behaviour

Polymers are sensitive to changes in temperature. Even small variations determine significant changes on the mechanical characteristics and behaviours, which depends on structure. The structure of polymer is defined in terms of crystallinity. Crystallinity is the order degree in solid’s structure. It has been calculated as the weight percentage of crystallinity state of the substance, compares to the total weight. Generally, the crystallinity degree is high in linear polymers and decreases in compounds with high branched or cross-linked chains. High crystallinity degree leads to greater packing of the chains consequently increasing in density, rigidity, hardness, resistance, and deformation (creep).

At solid phase, the polymer structure can be:

- *Amorphous polymer*: the chains (ramifications or lateral groups) arranged irregularly and are unable to pack in order, forming a “ball” structure. The random molecular jumble lets the chains move across each; the polymer may be easily deformed. For this reason, amorphous polymers have more flexibility and elasticity.
- *Crystalline polymers* have a very ordered arrangement, which gives strength and rigidity. Regular polymers can form lamellar crystals and crystalline substructures parallel in a certain distance from each other.
- *Semi-crystalline* polymers have both crystalline and amorphous regions. The solid in this case is more irregular having crystalline portion in the lamellae and amorphous portion outside them. Semi-crystallinity is a desirable property for most plastics because combines the strength of crystalline polymers with flexibility of amorphous and for this, can bend without breaking.

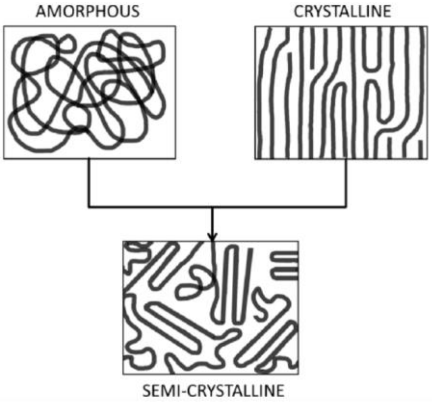


Diagram 2- Arrangement of molecular chains in crystalline, amorphous, and semi-crystalline polymers

The most useful classification of polymers is based on their thermal response. Under this scheme, polymers are classified as thermosets and thermoplastics.

- *Thermosets* have reticular structure which deny chains to detach ones from the others with temperature. Thermosets change irreversibly into hard and rigid materials once heating and cannot be reshaped. They are made from a liquid or soft solid substance that changes into an insoluble polymer by using heat or radiation. Thermosets will not soften upon heating, on the contrary they become harder. Thanks to this characteristic after initial heat forming, thermoset material's ability to exhibit resistance to heat, corrosion and mechanical creep make them perfectly suitable for components that require tight tolerances and excellent strength while exposed to elevated temperatures. These plastics were the earliest synthetic ones, tend to be rigid and have high molecular weights. This makes thermosetting plastics well-suited to production of permanent component with large and solid shape.
- *Thermoplastics*, despite the thermosets, are easily soften upon heating. This is due to the linear or branched-cross link chains where the primary bonds become weaker with temperature. The weaker intermolecular forces lead the material softens when exposed to heat and then returns to its original condition when cooled. Most linear and slightly branched polymers are thermoplastics. Thermoplastics cover a wide range of applications and are the most common on the market, usually the term simply referred to all plastics. Their features allow thermoplastics to be remoulded and recycled without negatively affecting the material's physical properties. Thermoplastics are high strength, lightweight materials and have relatively cheap processing costs. The primary disadvantages of using thermoplastics is the low melting point, therefore certain types can melt when just exposed to the sun or solvents.

Figure 1.4- Thermosets and thermoplastics polymers' characteristics

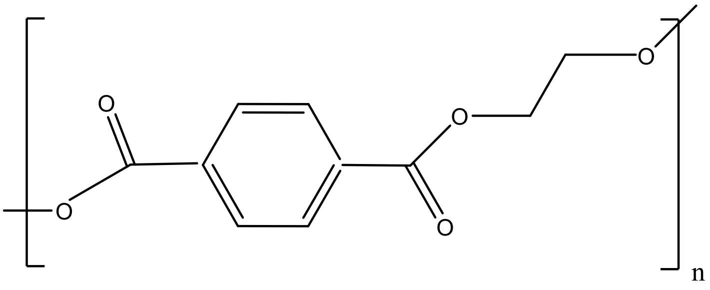
Property	**Thermosets**	**Thermoplastics**
Molecular structure	Network polymers: high level of crosslinking with strong chemical molecular bonds	Linear polymer: weak molecular bonds in a straight-chain formation
Melting point	Higher than the degradation temperature	Lower than the degradation temperature
Mechanical	Inelastic brittle, strong and rigid. Strength comes from crosslinking	Flexible and elastic. High resistance to impact. Strength comes from crystallinity
Polymerisation	Comprised of thermosetting resin and reinforcing fibre in its solid state	Comprised of hard crystalline and elastic amorphous regions in its solid state
Recyclability	Non-recyclable	Recyclable and reusable by varying heat and pressure
Solubility	Do not dissolve in organic solvents	Can dissolve in organic solvents
Cost	Cost-effective	Generally expensive
Examples	Epoxide (EP) Phenol-formaldehyde (PF) Polyurethane (PUR) Polytetrafluoroethylene (PTFE) Unsaturated polyester resins (UP) Polyesters	Polyethylene Terephtalate (PET) Polypropylene (PP) Polyvinyil Chloride (PVC) Polystyrene (PS) Low density polyethelene (LDPE) High density polyethylene (HDPE)

1.2. Plastic in the market

Despite the wide amount of plastics in the market, the Society of the Plastic Industry (SPI) established a classification system in 1988 to allow consumers and recyclers identify their different characteristics[3]. Manufacturers place an SPI code, or number, on plastic products, usually moulded into the bottom. The symbol numbered from 1 to 7 should provide to consumer some guidance on recyclability. Beside this classification, each plastic is associated with an abbreviation according to DIN 7728 and 16780 (as well as ISO 1043/1), which uniquely identifies it. The classification below shows the code logo and chemical structure of each plastic compounds.

1.2.1. Classification of plastics according to International Standards

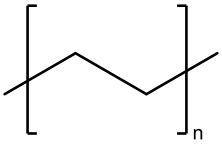
Polyethylene Terephthalate (PET) is the most common used plastics for consumer products (beverage bottles, medicine jars, rope, clothing). It is intended for single use applications especially packaging, because it absorbs odours and flavours from foods and drinks that are stored in them. Items made from this plastic are commonly recycled but not reused because repeated use increases the risk of leaching and bacterial growth. PET plastic is used to make many common household items.



Poly(ethylene terephtalate)
$(C_{10}H_8O_4)n$

Figure 1.5- Code 01 and chemical structure of Polyethylene Terephthalate (PET)

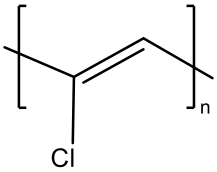
High-Density Polyethylene (HDPE) products are very safe and are not known to transmit any chemicals into foods or drinks. It is relatively simple and cost-effective process recycle it for secondary use. Items made from this plastic include containers for milk, motor oil, shampoos and conditioners, soap bottles, detergents, and bleaches. Even if HDPE is reusable, it is considered never safe to reuse an HDPE bottle as a food or drink container if it did not originally contain them.



Polyethylene
$(C_2H_4)n$

Figure 1.6- Code 02 and chemical structure of High-Density Polyethylene (HDPE)

Polyvinyl Chloride (PVC) is soft, flexible plastic commonly used for all kinds of pipes and tiles and blister packaging for myriad consumer products. PVC is relatively impervious to sunlight and weather. PVC is dubbed to be poison plastic because it contains numerous toxins which can leach during its life. This kind of plastic should not come in contact with food items as it can be harmful if ingested. Less than 1% of PVC is recycled.



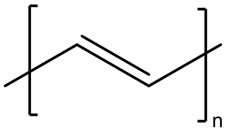
Polyvinyl chloride
$(C_2H_3Cl)n$

Figure 1.7- Code 03 and chemical structure of Polyvinyl Chloride (PVC)

Low-Density Polyethylene (LDPE) is considered less toxic than other plastics and safe for use. It is reusable, but not always recycled. It is a very healthy plastic that tends to be both durable and flexible. Items such as cling-films, sandwich bags, squeezable bottles, and plastic grocery bags are made from LDPE.

Figure 1.8- Code 04 of Low-Density Polyethylene (LDPE) (for chemical structure see figure 1.6)

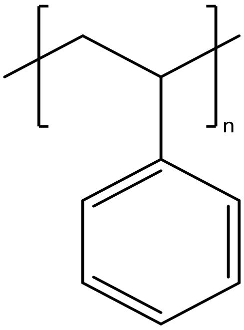
Polypropylene (PP) is strong and can usually withstand higher temperatures. It is occasionally recycled. PP is s to make lunch boxes, margarine containers, yogurt pots, syrup bottles, prescription bottles. Plastic bottle caps are often made from PP. PP is considered safe for reuse.



Polypropilene
$(C_3H_6)n$

Figure 1.9- Code 05 and chemical structure of Polypropylene (PP)

Polystyrene (PS) is inexpensive, lightweight, and easily formed plastic with a wide variety of uses (coffee cups, plastic food boxes, packing foam). Because PS's structure is weak, it breaks up easily and dispersed readily throughout the natural environment. As regarding human health, PS may leach styrene, a possible human carcinogen, into food products causing reproductive system dysfunction. PS is commonly recycled but is difficult to do. Polystyrene should be avoided where possible.



Polystyrene
$(C_8H_8)n$

Figure 1.10- Code 06 and chemical structure of Polystyrene (PS)

Code 7 (Other) is used to designate miscellaneous types of plastic not defined by the other codes. For this reason, reuse and recycling protocols are not standardized within this category. Polycarbonate and Polylactide are identified with "Code 7". One concern with this type of plastic is the potential for chemical leaching into food packaged in PC containers made using BPA (Bisphenol A) an endocrine disruptor. "O" plastics are difficult to recycle, reuse and compose.

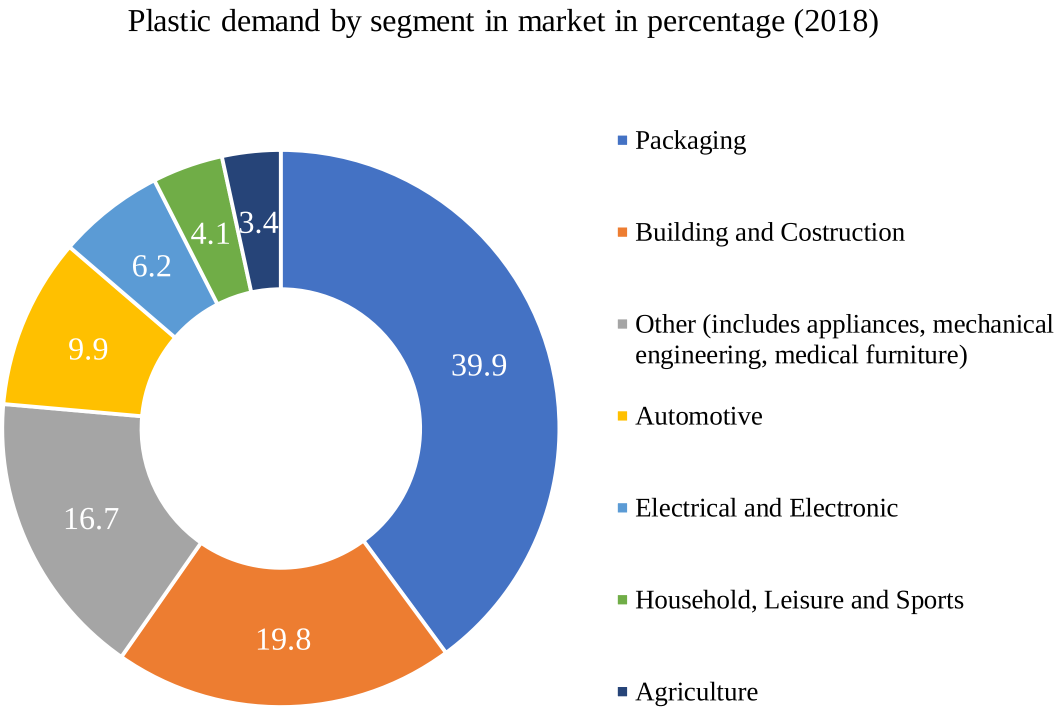
Figure 1.11- Code 07

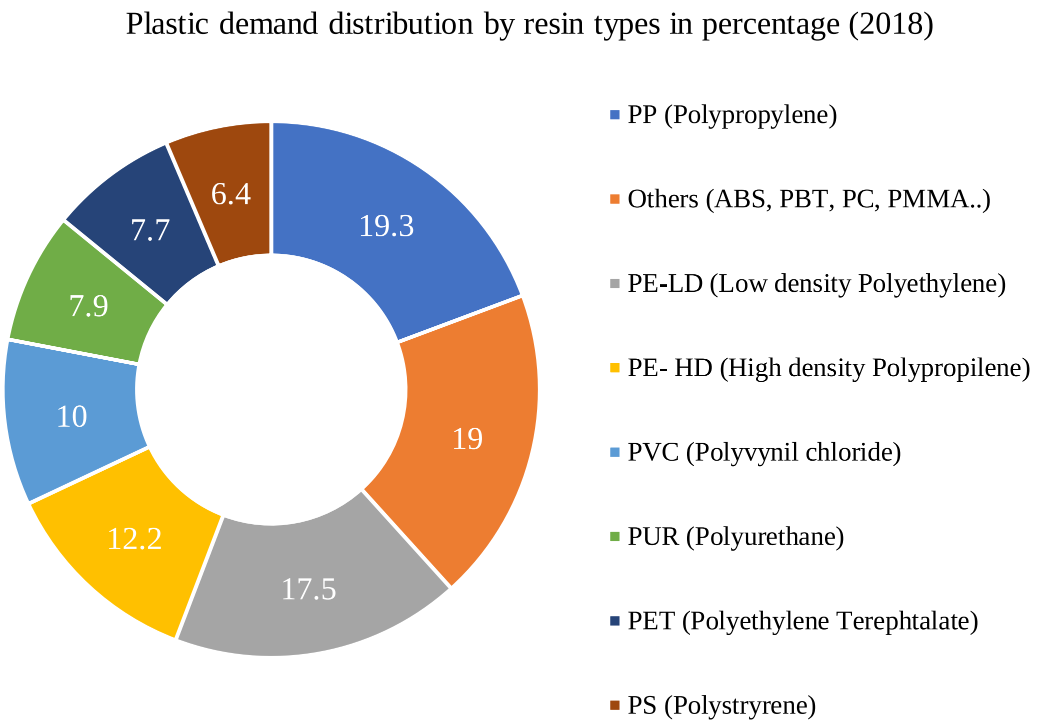
1.2.2. Plastic demand

Over the past 50 years, the role and importance of plastics in our economy has consistently grown. Global production of plastics has increased twentyfold since 1960s and it is expected to double again over the next 20 years. PlasticsEurope denounces in the latest report that global plastics production almost reached 360 million tonnes in 2018, 17% in Europe. The European Plastics industry had a turnover of more than 360 billion euros, by giving direct employment to more than 1.6 million people. The EU28 Member States' analysis includes plastics raw materials producers, converters, recyclers and manufactures[4].

Distribution of European plastics demand is divided in segments. The graphs 1.1 below show the distribution of plastic demand in 2018, in a total of 51.2 Mt. While Packaging (39.9%) and Building Construction (19.8%) by far represent the largest end-use markets, the Automotive industry (9.9%) is collocated at third place. 2017 showed the same trend; although the total quantity of plastic was the same (51.2 Mt), the Automotive sector held 10.1%.

The list of required polymers is driven by Polypropylene (PP) with its 19.3% of total.





Graphs-1.1 Market and distribution of plastic in Europe. The demand of plastic id divided by typology segmentation and distribution. Data are referred to the total 51.2 Mt of European Plastic in 2018.

1.3. Plastic waste management

Consumption, inevitably, leads to waste. In case of plastics, large volume of extremely persistent wastes is created. Sure is, that all plastic products become waste which are collected and treated.

To understand the life cycle of plastic products it is important to point out that not all plastics products are the same, with same uses and service life. Some are products themself and some are parts of an end-user product. According to the types mentioned, the end of life may come quicker or not, the lifespan may vary from 5 minutes to 50 years.

Currently, several end-of-life options exist to deal with plastic waste. There are three methods for plastic waste handling, each one with its own limitations. According to the Plastics Europe surveys, in 2018, 29.1 million tons of plastic were collected after its consumption: 32.5% of this quantity was recycled; 24.9 % went to landfills; 42.6 % was used to produce energy with waste-to-energy plants. Since 2006, the amount of plastic waste sent to recycling has doubled.

1.3.1. Incineration

Incinerators can provide or not energy recovery. Incineration’s revenues are heat and electricity production for municipal heating systems or steam for electricity. Plastic waste produces more than three times more energy when compared to other materials[5].

However, there is a significant trade-off in the incineration of plastics. Beside the ability to turn waste to energy, incineration converts materials into air pollutants: ash, combustion gases, wastewater, wastewater treatment sludge and heat by burning. Basically, since plastic are mostly made of petroleum and fossil resources, the incineration contributes to greenhouse gases emissions. Burning a metric ton of plastic in an incinerator results in almost one ton of CO_2 emissions. If the power generation potential had not been accounted for, the net CO_2 emissions would have amounted to 2.9 metric tons. Moreover, plastics contains hazardous chemicals in the form of additives that are released into the environment. Concentration of pollutants depending on how plastic waste is handled. It is important to point out that for highly mixed plastics, energy recovery may be the most suitable option[6].

1.3.2. Degradation and Landfill

Degradation of plastics is a very slow process; it can take 50 or more years for plastics to fully degrade. Natural degradation of plastic includes photodegradation, thermo-oxidative degradation, hydrolytic degradation, and biodegradation by microorganisms.

Generally, when a plastic is discarded, the subsequent degradation of the material occurs through a combination of biotic and abiotic mechanisms depending on the durability and composition of plastic and the environment in which it is disposed.

The abiotic factors are mechanical forces; light which exploits the photo sensibility of some materials and causes deterioration; chemical which is one of the most powerful abiotic degradative forces. It includes oxidation from atmospheric O_2, hydrolysis by H_2O and degradation caused by pollutants present in atmosphere.

In conjunction with abiotic factors, microorganisms (biotic factor) present in the environment such as bacteria, fungi, algae, can contribute to the biodegradation of plastic macromolecules.

All these degradative forces, biotic and abiotic, lead to the breakdown of plastic polymers.

Plastic deteriorates into fractions, fragments, debris and even microparticles which end, dramatically into environment. Landfill wastes from fossil origin have not been documented to emit greenhouse gases. However, landfilling poses significant environmental health risks due to toxic substances leaching into soil and freshwater. Landfills produce acids by decomposing organics and leach heavy metals out of plastic into the groundwater. Therefore, cannot be taken as long-term solution for plastic waste management.

Another drawback associated with disposal of plastic waste, is that landfill facilities occupy space that could be used for more productive activities (i.e. agriculture). Emissions from landfills could come from the transportation over long distance of waste. The significant environmental drawbacks of plastic disposal via both landfill and incineration were the driving force behind the development of plastic recycling processes.

1.3.3. Recycling

Plastics recycling is the physical process that recover material without altering the molecular structure of the polymers. Reprocessing waste plastic into useful products is more than three times efficient in terms of greenhouse gas emissions that manufacturing those same products with virgin raw materials. However, recycling rates for plastic are substantially lower than those for other widely used materials. Only some plastic materials can be recycled and, moreover only a fraction of "recyclable" used plastics is effectively recycled. The challenges are due to the use of colorants, additives and fillers during plastic production which can contaminate the recycling process. Additionally, each time plastic is recycled, virgin material is added to help increasing its quality. It is necessary to point out that plastic can be recycled twice or three times before its quality decreases, so the process only delays disposal into landfill or incineration.

The process of recycling plastics follows these steps:

1. *Collection***:** plastics are available in a wide number of forms.
2. *Sorting:* recycling mill sorts the scrap plastic by symbols at the bottom of the plastics. The most common recycled plastics are Polyethylene Terephthalate (PET), Polyvinyl Chloride (PVC), High-density Polyethylene (HDPE) and Low-density Polyethylene (LDPE).
3. *Shredding*: the next step is cutting the plastics into tiny chunks or pieces.
4. *Cleaning***:** the flakes or chunks are then washed with detergents to remove the remaining contamination. The plastic flakes are then subjected to moderate heat to dry them.
5. *Melting:* material can be melted down and moulded into a new shape or they are melted down and processed into granules.
6. *Making of pellets:* the plastic pieces are then compressed into tiny pellets. In this state, the plastic pellets are ready for reuse or be redesigned into new plastic products. It is

important to point out, that recycled plastic is hardly used to make identical plastic item as its previous.

There are two approaches currently in widespread use for the recycling: mechanical and chemical. Mechanical recycling can be closed cycle (primary) when uncontaminated plastic is directly recycled, or cascade recycling (secondary) where post-consumer plastics are sorted and purified and then recycled. However, the heterogeneity of plastic products and different recyclability degrees make the processes difficult in many cases. The chemical, or feedstock, recycling describes innovative technologies where plastic waste is converted into valuable chemicals. These technologies include pyrolysis, gasification, chemical depolymerization, catalytic cracking and hydrogenation. Chemical recycling should see as complementary solution to mechanical recycling.

1.3.4. Best plastic waste management

Generally, choosing the best waste management option might be tricky. The comparison lays on multiple and dissimilar key variables such as: material, product, design, local waste management system and policies.

Plastic waste management is something that needs to be looked at individually terms. Environmental, economic, and social factors weigh up and prioritise in decision making process. Considering a comparison between Incineration, Landfill and Recycling processes, this last seems to be the most virtuous management amongst the cited. It is almost impossible finding a pro that wipes out all cons. In fact, recycling plastics delays, rather than avoids final disposal. Studies estimate that only 9% of total plastic produced in the last 50 years have been recycled, 10% of which recycled more than once[7]. Furthermore, it should not be forgotten that the profitability between recycling plastic and production of new one is strongly determined by oil prices.

The benefit of recycling is the avoided CO_2 emissions that would otherwise be released during incineration and production of virgin plastics. At the same time, there are process' steps (collection, separation, sorting, etc) which could contribute to the pollution and to increase the operational costs. Economically, operating costs for recycling are still prohibitive due to the expensive technologies and maintenance costs for plants. However, developing recycling can be an engine for job's growth (i.e. reinternalizing employment within territory).

1.4. Plastic in environment

Plastics are undeniably a key environmental concern, in terms of impacts to ocean, health and wildlife.

Plastic is produced from petroleum or natural gas. These feedstocks are the end-product of millions of years of natural decay of once-living organisms and are themselves natural products of environment. Although it appears that plastics seem to be natural in their origin, the chemical process used to make them are artificial. The starting consideration for understanding plastic behaviour in environment, is that the chemical configuration of plastic is what determines its properties. From this phrase, it is reasonable why nature is not suitable to decompose plastic, making it long lasting in ecosystem.

Due to plastic's resilience against degradation and its proliferation in industry, the issue of plastic pollution has evolved to become a threat. Plastic pollution arises from both terrestrial and marine sources due to its properties of buoyancy and durability. The continuous stream of plastics is maintained via two means: purposefully, though illegal or inappropriate dumping of domestic and industrial waste, and inadvertently.

It is important to stand out, that release of pollutants associated with plastic may occur in all phases of plastic life cycle (from production, use, to end-of-life). During production, a huge quantity of dangerous chemical gases is released into the atmosphere. Contaminating air means affect all organisms on planet. During the use, plastic can break leaving some toxicants molecules. These may be volatile or not and can affect indoor and outdoor environments. Moreover, plastic is an absorption material, making it a carrier for toxicants and chemical compounds.

When plastic becomes physically waste, it causes several hazardous and ecologically damaging effects. Plastic debris poses a direct danger to fauna by ingestion, inhalation, interaction, and entanglement. When degradation, photodegradation and other weathering process make plastic fragments microscopic, the hazardous become invisible, silent but worst. The relatively modest amount of climate research has focused primarily on the impacts of plastic and microplastic within oceanic environments and aquatic ecosystems.

1.4.1. Plastic in the ocean

Until recently, the researches on plastic pollution in the ocean have focused on its global abundance, distribution, and ecological harm. Marine pollution is a growing and visible problem in today's world. Using a validated model, Eriksen et al. (2014) estimated that the total number of floating plastics pieces, divided into four size categories, was 5.25 trillion with a mass over 250000 tonnes[8]. Plastic represents more than 80% of the waste in the oceans. Ocean is being flooded with two main types of pollution regarding plastic dimension: micro and macroplastics. If the currently production and use of plastic remains the same, UNEP (United Nations Environment Programme) estimates that by 2050 there is more plastic (by weight of thousands of tonnes) in the oceans than fish[9]. Plastic's journey from sources on land, from creation to waste, is promoting by natural and humans' transporters.

Plastics in marine environment pose incalculable and irreparable damage to marine ecosystems and animals who living in them. First problem highlights when fishes become tangled and injured in the debris and some animals mistake these items for food by eating them. By passing of time, plastic breaks down in all shapes and sizes, where those less than 5 millimetres in length are called microplastics.

Microplastics term arises in 2004 to describe fragments with diameters down to ~20 µm, which have been detected in a range of marine species including plankton and whales. These dimensions give the potential to cause harm to biota. Microplastics consist of carbon and hydrogen atoms bound together in polymer chains. Other chemicals compounds, as in conventional plastics, are present in microplastics too and may leach out. Among microplastic, nanoplastic particles (<1µm) are concerning for dimensions. Microplastics are divided into two types according to origin:

- *Primary* is all plastics that are manufactured to be of a microscopic size. These plastics are designed to be included typically in personal care products and cosmetic products (PCCPs). The term microbead is referred to many health and beauty products (such as scrubbers and toothpastes). Primary microplastics enter directly in the environment through any various channels (wastewater system from households).
- *Secondary* microplastics describe tiny plastic fragments derived from the breakdown of larger plastic debris, both at sea and on land. Over time, a mix of physical, biological, and chemical processes can reduce the structural integrity of plastic resulting in fragmentation.

Both types of plastics will be subject to similar processes when in the environment. Due to their chemical nature, primary and secondary microplastics accumulate and persist. The microscopic dimensions permit to microplastics to have been found in digestive tracts and tissues of various invertebrate sea animals. It is demonstrated that microplastics are working their way up the marine food chains, from zooplankton and small fish to large marine predators. Since presented in water, microplastics are captured unintentional and collected inside the organisms, especially in tissues and organs.

The ingestion of microplastics can cause to aquatic species a decrease in consuming suitable food and this, leads to have less energy to carry out normal life functions. It can result a weak neurological, immune, and reproductive systems which could induce to extinction. Field studies demonstrated that commercial fish species, both pelagic and benthonic normally ingest microplastics. Many bivalves and mussels are filter feeders and are likely to be the most exposed to higher concentrations of microplastics than mobile organisms. At moment significant elements point out cellular effects associated with intake, which include alteration of immunological responses, neurotoxic outcomes, and onset of genotoxicity. All reactions are still studied in experimental set-ups, in which concentration of microplastics may be much greater than might be experienced under more natural conditions. Additionally, researches are growing for better understand the implications on animals and consequently on human health. Since the food chain ends with humans, microplastics pollution may migrate up to the top predator who suffer of all negative impacts accumulating in the previous levels. It is evident that humans are exposed to microplastics through their diet. Consumption of filter feeding invertebrates such as mussels and oysters, are the most likely route of exposure to microplastics but a wide variety of other commercial species appear to be contaminated as well. Understanding mechanisms and real toxicity of microplastics in humans constitute one of the major knowledge gaps to overcome in the next years.

Chemical contamination is less obvious, but not for this reason less dangerous.

This type of pollution occurs principally when human activities lead to the runoff of chemicals into waterways that lastly go into the ocean. The increased concentrations of chemical (mostly derived from agriculture with pesticides), such as nitrogen and phosphorus in the coastal ocean promote the growth of algal blooms. Harmful algal blooms, or HABs, occur when colonies of algae grow out of control producing toxins that can kill fish, mammals and birds and may cause human illness or death in extreme cases. The overfeeding of algae takes place when nutrients (P, Ni and C) from human activities, such as farmlands, flow downriver to the sea and build up fodder to algae that normally survive in environment with nutrients around them.

The negative effects caused by algal blooms have been reported as sluggish water circulation, unusually high temperatures and extreme water events (hurricanes, floods, and drought). HABs hurts human health with breathing problems, when toxins presented in shellfish are eating. In economic terms HABs affects local fishing and tourism sectors.

Besides microplastic, the impact of marine pollution on individual animals is more evident when dealing with entanglement in floating debris, very often related to fishing gear. This is a global problem that affects all higher taxa of individuals. Incidents have been widely reported for marine mammals, reptiles, birds, and fish. In many cases this leads to acute and chronic injury or death (asphyxiation, entrapping). In the same way as microplastics, macroplastics can cause problems when ingest. Seabirds appear to be particularly susceptible at mistaking plastics for their natural prey. Evidences are shown in turtles and toothed whales' stomachs, where frequently are found to have large quantities of plastics. The compartments' physiology of these animals makes it extremely difficult to eliminate the material once entered. Wastewater provides a pathway for dissolved chemicals as well as solid particles to be transported into aquatic habitats. Large solid items enter the wastewater system via toilets (nappies, tampons, contraceptives, and cotton buds). Theoretically these should be removed by primary sewage treatment which prevent their entry to the environment. However, in conditions of heavy rainfall the system can become overwhelmed by the volume of water and materials can escape to water courses untreated via overflows. To prevent the removing of these materials, it would be possible to introduce more effective filters for both micro and macroplastics. However, the justification might be difficult to make in term of cost-benefit. Till now, this type of treatment is relatively expensive for many countries and municipalities and may only be carried out when there is a sensitive habitat or more solid question of human health involved.

1.4.2. Plastic and human health

Humans come in contact with plastic in all stages of its lifecycle: from the extraction of raw materials to the manufacture of plastics, through to consumer usage, and finally their disposal. Most plastics' chemical characteristics are harmful to humans and the invisibility to the naked eye, make these materials even more dangerous. Several studies have found links between plastic and problems across the human body's system: such as cardiovascular, respiratory, reproductive, and gastrointestinal apparatus. Therefore, the health impacts can be possibly reflected as cancers, chronic inflammation, and various immune diseases. Studies declare that there are still uncertainties and knowledge gaps which undetermined a complete evaluation of both acute and long-term health risks at all passages in plastic lifecycle. Impact on plastics is hampered by limited information but always more attention is putting on the theme.

When considering impacts of plastics on human health, it is possible to separate direct and indirect exposure. The results differ from the way in which plastic particles (micro-nano plastics) and toxic chemicals can enter in human body through inhalation, ingestion, and direct skin contact. Moreover, other variables are important such as duration of exposure, dose, mixture of chemicals and vulnerability of individual (sex, age, pre-existing health conditions, history of environmental exposures).

Today, pollution is the largest environmental cause of death and disease. The principal factor is directly linked to air pollution, which has been identified as the most pervasive environmental threat on human health. This is due to multiples ways that plastics impact air quality: extraction of raw material (oil), incineration and plastics ability to "off-gas". Beside plastics, it is important to consider the chemical compounds intentionally added for improving their characteristics. These compounds have many structural qualities like flexibility and heat resistance which lead them to be even more harmful. Additives, plasticizers, pigments, flame retardants and fillers are added to plastics and intended to be most durable and persistent as possible.

Since associated later to plastic, they are not strictly bound to the polymer matrix, and for their low molecular weight can easily leach out of polymers into the surrounding environments (air, water, food, or body tissues). As degradation of particles is continuing, new surface is exposed, allowing further leaching process. Evidence of toxic and ecotoxicological effects caused by plastics and chemical compounds have been investigated on human population.

Researches show that many of the plastics' particles in human bodies come from the air breathed. Thanks to small dimensions, particles can enter via nose and mouth in the respiratory system. The inhalation of small size particles is abundantly present in both indoor and outdoor air. The smallest compounds can penetrate the bloodstream and cause cardiovascular and cerebrovascular diseases. Presence in lung and muscular tissue, demonstrates the bio-persistence of these substances and confirm the body's inability to rid itself of them. BPA, phthalates, brominated flame retardants and many organic contaminants act as endocrine disruptors chemicals (EDCs). These chemical compounds mimic the natural hormone behaviours and have the capacity to interfere with hormone receptors, hormone synthesis and hormone conversion. They show health problems to neurological development and endocrine system like genital malformations, lower testosterone levels production, decreased sperm counts and reduced female fertility. Effects are more evident in vulnerable populations, such as children and pregnant women. Especially for pregnant women, such impacts on developing fetus have been shown to increase the likelihood of birth defects of the brain, heart, and spine.

The uptake of plastic particles by humans can occur through the consumption of terrestrial and aquatic food products. In animals, first study of plastic trophic transfer came about almost a decade after discovery in sea lion scats. A recent study suggests that an average person could be ingesting approximately 5 grams of plastic every week[10]. Studies highlighted a list of common food and beverages containing microplastics, however water represents the largest source of contamination. In fact, mismanagement of microplastics may be accumulated and transfer through the food chain reaching human digestive system. Additionally, high levels of organic pollutants and toxic chemical (PAHs, PCBs), within and adsorbed to microplastics, increase risks associated with bioaccumulation at higher level of trophic chain. Evidences for the trophic transfer of microplastics are results of both bioaccumulation and biomagnification. While Bioaccumulation is just accumulation of toxins and chemical in an organism, Biomagnification is the concentration of toxins and chemical substances in an organism due to consumption of other organisms that contain such toxin/chemicals. For this reason, biomagnification potentially poses a direct risk to human health. In animals, differences in feeding mode and ingestion behaviour substantially affected bioaccumulation potential.

Researches are mostly focusing on accumulation in lower trophic levels, in order to better understand the mechanisms and problems related to all food webs. However, with a lack of robust data describing predator-prey for microplastics and associated contaminant transfers, knowledge is still insufficient to inform a risk assessment of microplastics in environment and the implications that may exist for some food.

1.4.3. Finding solutions based on transparency and participation

Extreme lack of transparency around some chemical compositions and the production processes through which plastic is produced, prevents the totally understanding of exposure to risks and a full assessment of impacts. This is powered by the treatment of confidential business information and inadequate disclosure requirements. These gaps reduce the ability of:

- Regulators to develop right safeguards
- Consumers to make informed choices
- Frontline communities to limit their exposures to plastic-related health hazards and respond properly when emergencies occur

There is an urgent need to solve the plastic pollution problem. First performing development in research on potential health risks, whilst drastically limiting its production and usage. Despite remaining uncertainties, existing information about the severe impacts of the plastic lifecycle justifies the urge to apply a strong precautionary approach.

Another important step is educating public on these issues. Therefore, transparency will be the key to lead people making fully informed lifestyle decisions and limit their exposure to these pervasive, harmful substances. With REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) the European Union engages to improve the protection of human health and environment from the risks that can be caused by chemicals. REACH enhances identification of the intrinsic properties of chemical substances. Institutions might design regulatory instruments to mitigate the effect of plastic during its whole lifecycle. Waste legislation and policy of the EU Member States is based Directive 2008/98/EC[11]which introduces waste management and waste preventions plans. Moreover, the individually citizens participation is fundamental to make steps towards reducing the problem. Changing the behaviour of people's in terms of plastic usage in the daily activities is not immediate and need effective education. People's commitment is let by increasing respect and consciousness for human rights to health and to a healthy environment. Actions based on organization, commitment and effort lay the groundwork in 3Rs behaviour's programme. Key components follow this easy hierarchy and help to be aware on consumer's power:

- *Reduce* to effectively using fewer resources in the first place. It is the most effective of the 3Rs, as well as the starting point. Reduce as trying to refuse plastic.
- *Reuse* is the consumer's consideration on how can be done more with products. Reuse makes economic and environmental sense and takes creativity.
- *Recycle* is a series of regulated steps that need an already used material in order to be processed, remanufactured and sold as a new product.

1.5. Plastic new strategy

European Commission is strongly committed into issues related to plastic materials production and plastic waste management. The Plastic Strategy adopted by the Europe in 2018 is an integral component of the Circular Economy Action Plan (2015), putting plastic in a circular logic. The need for an economic approach becomes clearer when considering importance of plastic in European economy.

The circular economy is an alternative to the current linear, make, use, dispose, economy model. Circularity aims to keep resources in use for as long as possible, to extract the maximum value from them already in use and to recover and regenerate products and materials at the end of their service life. The circular economy promotes a production and consumption model that is restorative and regenerative by design.

Circular economy transition would result in a snowball effect by positively impacting human lives and health, saving natural resources, reducing Europe’s dependency on foreign resources, and boosting creation of greener industries, jobs, and technology developments.

The Ellen MacArthur Foundation summarised the goals for a circular economy in the plastics sector with three main ambitions[12]:

- Create an effective after-use plastics economy by improving the economics and uptake of recycling, reuse, and controlled biodegradation for targeted applications. The European plastics manufacturers are committed to ensure high rate of reuse and recycling with the ambitious to reach 60% by 2030.
- Drastically reduce leakage of plastics into natural systems (particularly the oceans) and other negative externalities.
- Decouple plastics from fossil feedstocks by exploring and adopting renewably sourced feedstocks.

These goals might be achieved with examples of actions and tips as:

- Embrace sustainable business models which promote products as services and encourage the sharing and leasing of plastic products. Thereby optimise product utilisation and decreasing the volume of manufactured goods.
- Increase collaboration between businesses and consumers to increase awareness of the need for, and benefits of a shift from non-essential plastic use and a throw-away culture, to encourage recycling, and to increase the value of plastic products.
- Develop robust information platforms which provide data on the composition of plastics, track the movement of resources within the economy.

- Implementing economic, policy and regulatory measures such as taxes, extended producer responsibility, mandatory requirements and standards for circular/eco-design while banning certain plastic types.
- Redesign plastic manufacturing processes and products to improve longevity, reusability, and waste prevention, by incorporating after-use, asset recovery, and waste and pollution prevention into the design from the outset
- Use plastic waste as a resource, remanufacturing of new plastics or conversion into other valuable products.
- Produce plastics from alternative feedstocks including bio-based sources such as sugarcane, oils, cellulose, sewage sludge, food waste and natural occurring biopolymers.

Limitations of natural resources and growing world population are concerning even more. Topics as sustainable development, resources availability, global climate change and waste reduction are increasingly dominating political and industrial agendas. The 2030 Agenda for Sustainable Development Goals (SDGs) was adopted in 2015 by all United Nations Members States as universal call to act[13]. Among the seventeen points, SDG 12 handles the materials consumption. To meet this goal, plastic's problem can be partly overcome by finding substituted materials. "Responsible consumption and production" perfectly fit the urgent actions necessary to explore the availability and versatility of biological feedstock.

Transition to bioeconomy is one of the biggest industrial challenges of the 21st century. To be successful, the European bioeconomy needs to have sustainability and circularity at its heart. A sustainable bioeconomy is the renewable segment of the circular economy. Bioeconomy pushes to activate the potential of biobased materials. A scaled-up and strengthened bio-based sector can do more than non-renewable substitution: it can support the renewal of the EU industrial base; it can contribute to the greening of industrial products; and it can help to systematically turn bio-waste and discards into value, thus achieving circularity.

Bioplastics are an important part of the bioeconomy and will drive the future of plastics chain.

1.5.1. Biological feedstock

Bioplastic is made by fermentation or chemical polymerisation of raw materials which are generally carbohydrates, sugars. A distinction should be made between crops from which sugars are easily extracted (direct), such as sugar cane, sugar beet and corn and those from which sugar extraction is technically more difficult, for example lignocellulosic crops. The extraction of sugars from lignocellulosic biomass still represents a challenge to the bio-based industries. The industry particularly ais to further develop fermentation technologies that enable the use of lignocellulosic feedstock sources in order to not use only food crops but agricultural waste materials as well. Land use is a feature of remarkable importance in life cycle of bioplastics. Many discussions are focused on the competition for land used to produce biofuels and biomaterials and feed production. However, it is estimated that globally just 2% of cultivated land is dedicated to biofuels and only 0.1% to bioplastics. Therefore, bioplastic's impact on food and feed production is extremely small. Bioplastics' production has changed over time thanks to technical development and market demand. This can be seen in terms of three generations which are existing in the same meanwhile.

- *First generation (food)* includes the first crops and plants used to produce bioplastics. Feedstock are most efficient to production as they require less land to grow and have a higher yield compare with other generations. There are more subjected to criticism because of its potential competition with food and animal feed. In fact, they take away food destinated for human or animal consumption. Examples of food are divided into vegetable oils (soybean, palm, sunflower, colza), starch (corn, potato, wheat, tapioca) and glucose (sugar cane, beetroot).
- *Second generation (non-food)* is an improvement of the first in terms of performance. Second generation feedstock can be either cellulosic feedstock wood, waste material from agriculture) or waste material from 1st generation (i.e. waste vegetable oils and castor beans). Biomaterial from 2nd generation have increased characteristics by reaching industrial scale production.
- *Third generation (non-food; soil-less farming)* considers problems generated with the previous generations. Feedstock are sugars or oils produced by micro-organism (micro-algae, bacteria, mushrooms) or municipal waste material (organic waste, wastewater).

Renewable feedstocks are an alternative solution that allow the creation of new pathways between the fields of agriculture, chemistry, and technologies by keeping the approach of sustainable management of natural resources. Using vegetable biomass as a replacement to fossil sources, the released CO_2 can be at least minimized by plant CO_2 consumption during photosynthesis, reducing the carbon footprint in the global atmosphere. The advantages can be addresses firstly to fossil fuel savings and reduction of greenhouse gas emissions in atmosphere. However, end-of-life options are major considerations for bioplastics. Nowadays, real big issues of plastic are its big quantity and management. Thanks to properties of bioplastic as biodegradability and/or compostability there is the possibility to better handle waste.

2. BIOPLASTIC

Bioplastics is a family of materials with different properties and applications, which derive from renewable resources. With renewable resource means natural resources in which exploitation rate does not exceed replenishment by natural processes. The prefix “bio” in bioplastic, is mostly used to indicate the origin but could express “bio” functions as well.

Bioplastics may be either biobased, biodegradable or have both properties. Their production releases fewer greenhouse gases emissions (GHG) than conventional plastics and for this reason are considered environmentally friendly materials or carbon neutral ones.

The term bio-based refers to a material or product totally or partially derived from biomass such as plants, trees, or animals (the biomass can undergo physical, chemical or biological treatment). Mostly plants are annual crops such as corn, sugar beets or perennial cultures such as cassava and sugar cane.

Biodegradability refers to chemical process during which microorganisms present in environment, transform materials into natural substances such as water, carbon dioxide and biomass. Definition of biodegradable plastic still have contradictions. The easiest explanation defines biodegradable plastic suitable to biodegradation.

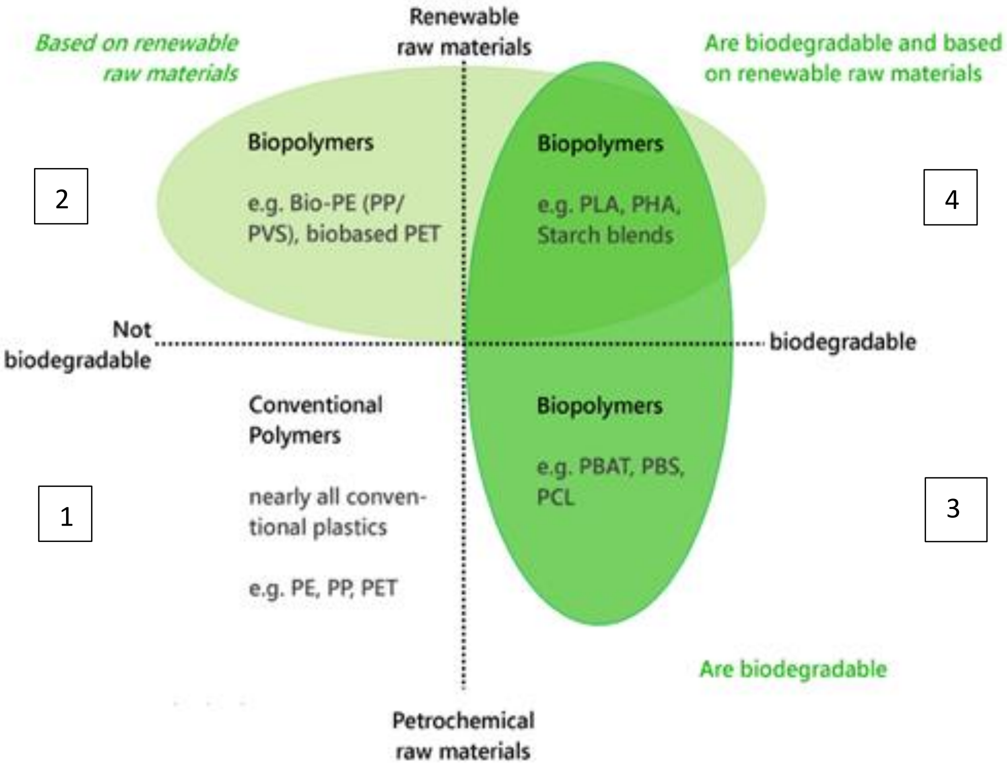
The process of biodegradation is closely linked to the molecular structure of the polymer, it does not depend on the origin of the material. The mechanism takes place when the microorganisms in the environment (e.g. bacteria, fungi, algae) recognize material as food, and start the process of consuming and digesting. Biodegradation is composed of many sequences. Fragmentation is the first phase followed always by mineralization. Mineralization is the process that converts organic carbon into inorganic carbon. If only fragmentation occurs, it means that the material is degraded, if mineralization follows as well, it means that material is biodegradable

Figure 2.1- Illustration of difference between degradation and biodegradation

Biodegradation can occur in both aerobic and anaerobic conditions. In the first case, the products of biodegradation are carbon dioxide, water, and biomass. In anaerobic conditions the products are methane and biomass. Among the different biodegradation processes, composting can be one. The term compostability stands for a controlled treatment of material carried out only in aerobic conditions.

2.1. Types of materials

In order to illustrate classification of biomaterials, European Bioplastics[14] has introduced two-axis model in which all type of plastics, and their combinations, are inserted. The graph 2.1 below shows the material coordinate system of bioplastics.



Graph 2.1- Material coordinate system of bioplastics

According to this classification, there are four type of plastics.

The horizontal axis distinguished biodegradable and non-biodegradable polymers, while the vertical axis plastic derived from renewable sources and petrochemical materials.

1. No-biodegradable plastics of petrochemical origin, including all the conventional ones.

2. Biobased or partly biobased, non-degradable plastics such as biobased PE, PP, or PET. They are chemically similar to conventional polymers with the same technical characteristics. They can easily and immediately replace their petrochemical equivalents.
3. Plastics based on fossil fuels resources and are biodegradable such as PCL. They are comparatively small group and are mainly used in combination with other bioplastics for improving the specific biodegradability performance and mechanical properties.
4. Plastics that are both biobased and biodegradable, such as PLA, PHA, PBS and TPS. These materials have new chemical structures, properties and thus is necessary to select them depending on the characteristics expected from the final product. Since are recent to industrial scale operations (less than 10-20 years for most of them), they need research and development to improve their qualities and adapting them to market expectations.

Bioplastics, therefore, encompass three of the four groups presented differences between materials that are either bio-sourced or biodegradable, or both. Other terms appear on the plastic market (oxo-degradable, oxo-fragmentable, bio-fragmentable, oxo-biodegradable) but are not considered bioplastics. The applicable standard which defines bioplastic is met in EN 13432.

2.1.1. Label on Bioplastic

Biomaterials sector is growing in the recent years. However, there is still large amount of misleading information about so-called “green products”. The environmentally conscious on the part of customers pushes to a need for a transparent, easy understandable guarantee of products. To overcome this request, standardization bodies have developed specific rules for bioplastics.

Currently, there is no obligation for producers to certify products, companies can provide information on a volunteer basis. The certifications offer a tool for fair play in the market of bioplastics. Compostable, biodegradable, and biobased products investing on credibility by providing clarity to consumer. The label on the final products has the aim to define technical specifications on origin and future treatments at the end of life. There are two main groups of standards:

- *Standard specifications*: “pass/no pass” requirements which a product or service must satisfy to obtain label. Standard specifications are often the basis of certification schemes.

- *Test methods*: evaluation techniques that describe how to carry out the tests and how to validate them. The test method meets regulations indicated in the standard specification.

2.1.2. Competent Authorities

The certifications and labels are confirmations that a product overcomes the standards' requirements. Standard and rules are set by international bodies, such as:

- ASTM American society for Testing and Materials (USA)
- ISO International Organization for Standardization
- CEN European Committee for Standardization (European Union)

The main certification bodies for bioplastics in Europe are DIN CERTCO and VINÇOTTE.

The DIN (Deutsche Institut für Normung) CERTCO system is adopted by Germany, Switzerland, the Netherlands, the United Kingdom and Poland. It mostly certifies products made of compostable plastic.

On the other hand, VINÇOTTE certifies plastic suitable for home composting and biodegradability. The system operates internationally through offices located in Belgium and Italy.

Since 2007, in Italy compostable products have been certified by CIC (Italian Composting Committee) following the checks carried out by Certquality.

What is "Biobased"

The term means that the material or part of product derived from biomass. The method to determine the "biobased" as a characteristic, are detailed in specific standards of CEN/TC 411[15].

Presently, most biobased materials are sourced from plant-based raw sources like traditional crops as corn and sugar cane (1st generation, food). However, many researches are moving to other feedstocks including agricultural or forest waste (2nd generation, non-food), and municipal waste (organic, water) as well as algae and mushrooms (3rd generation, non-food; soil-less farming).

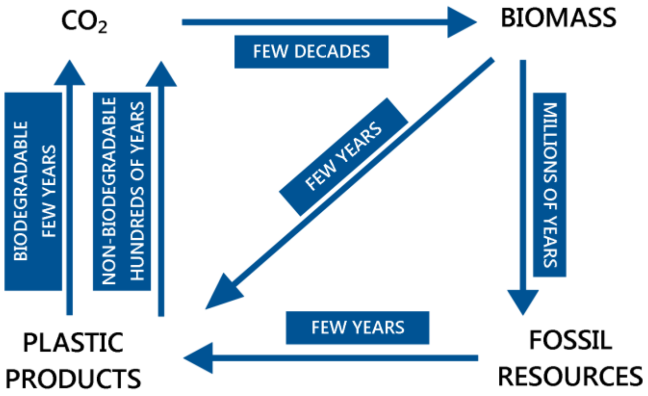
The biobased content of a bioplastic can be reported and certified in several ways.

Standards and methods

The most common method for measuring biobased content is expressing the weight-percentage of renewable resource in the product.

Another way is the percentage calculation of biobased carbon content. The total quantity of organic carbon is measured using the *ASTM D6866*[16] test method specification (Standard Test Methods for determining the Biobased content of Solid, Liquid and Gaseous Samples using Radiocarbon Analysis). Through radiocarbon dating, it is possible to determine the carbons obtained from renewable resources in a material, compared to the carbons obtained from fossil fuels. The analysis of bio-based content is done with calculation of isotope 14-C (carbon 14). The isotope has the properties to be unstable and decays slowly. The unicity is its constant value and presence in organisms. Natural compounds and biomass have higher concentration of 14-C, comparing with petroleum-based materials.

Figure 2.2 shows the carbon lifecycle. The age of carbon indicates the time required to obtain the necessary carbon for the production. Conventional plastics produced from fossil resources, have carbon generated over millions of years (old carbon). On the other hands, the bio-based plastics contain carbon that has been circulated in nature for less time (new carbon). The biobased measure is basically, the relationship between the “new-carbon” and “old-carbon”.



Graph 2.2- Illustration of simplified carbon cycle (Ramani Narayan)

Beside the ASTM D6866, Europe adopted *EN 16785-1: 2016* standardization[17]. This European standard allows the determination of biobased content through a radiocarbon and elementary analysis. It is more detailed because involves not only the biobased carbon content, but also other elements as oxygen, nitrogen, and hydrogen.

The system may be used for products, totally or only partially derived from materials/polymers/resources of natural origin. The certification may be applied only to non-toxic and non-medical products. To be certified as bio-based, the product must contain:

- At least 30% of the total organic carbon of dry matter
- At least 20% of carbon from renewable resources

Certifications

United States Department of Agriculture (USDA) Program accredits with label (figure 2.2) on products the percentage of biobased content. The certification can be mandatory or voluntary. The label guarantees that product have submitted test evidence to USDA and ASTM D6866.

Figure 2.2- USDA certificate (Source: Biopreffered website)

In Europe certifications are provided by two organisations which corresponding labels according to the American standard.

VINÇOTTE certificate with *OK biobased* label, which grants four seals differing in the number of stars. Each star (from one to four) represents the percentage of biobased content calculated according to the American standard ASTM D6866.

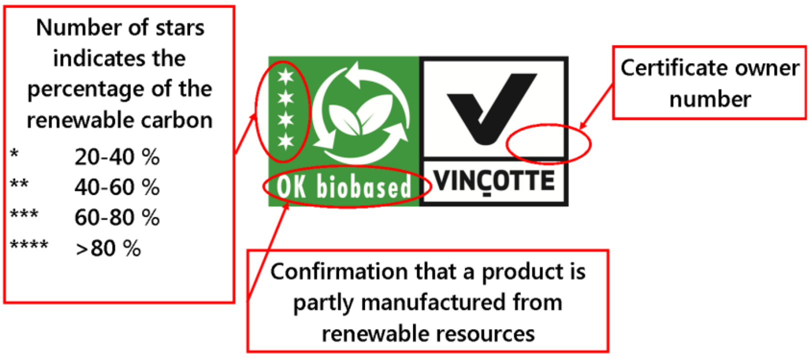


Figure 2.3-Vinçotte certification label for products from renewable resources (Source: Vinçotte website)

DIN CERTCO with "DIN-Geprüft biobased" mark determines and certifies the biobased carbon proportion in a product. The certification scheme is based on ASTM D6866 standard as well and provides classification in three bands according to percentage of bio-based content (20-50%, 50-85%, >85%). The certificate is valid for five years and is also regularly monitored.

Figure 2.4- Certification labels for products deriving from renewable resources (Source: website DIN CERTCO)

What is "Compostable"

Composting is the process of breaking down organic waste by microbial digestion, in order to create "compost" without producing toxic residues. A final compostable material is biodegradable, because composting is a controlled, accelerated form of biodegradation. Intermediate products can obtain registration or certificate of conformity to a standard, but not the labels. Composting is a regulated process and requires the right level of heat, water, and oxygen.

Standards and methods

ASTM D6400 (American Society for Testing and Materials)[18] defines specifications for labelling plastics that are originally designed to be aerobically composted both in municipal and industrial facilities.

EN13432[19] is the European Standard which defines characteristics of material to be biodegradable or compostable.

According to this standard, a material should be considered compostable if has these peculiarities:

- *Degradability*: at least 90% within six months (180 days) in the presence of an environment rich in carbon dioxide. The value must be verified according to ISO 14855 method.
- *Biodegradability*: at least 90% of polymer mass must be converted into carbon dioxide within six months (180 days).

- *Disintegration analysis* must be done during biological treatment. The analysis carried out after three months (12 weeks) of industrial or semi-industrial treatments must reveal a sufficient level of disintegration (residues with dimensions below 2mm).
- *Eco-toxicity analysis*: biological treatment must not have negative effects on the composting process.
- *Chemical composition analysis*: heavy metals, pH, saline content, N, P, Mg, K concentration must be respected, following the limits shown in Annex A of the standard. Low levels of contamination may be acceptable but there must not affect the quality of the compost.

Certifications

Both DIN CERTCO and VINÇOTTE, release the compostable marks registered by European Bioplastics which guarantees compostability and biodegradability.

The Compostable CIC mark identifies and certifies all products that naturally decompose in composting process and have the characteristics of biodegradability and disintegration established by European standards (UNI EN 13432:2002).

Seedling-label means that the product will fully biodegradable in an industrial composting plant under controlled conditions (temperature, moisture, and time), leaving nothing behind water, biomass, and CO_2.

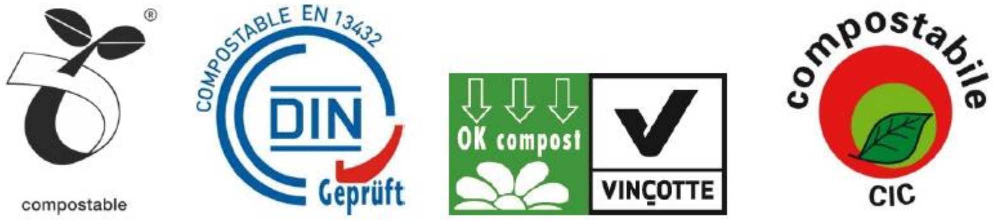


Figure 2.5- Different brands certify with own logo the compostability of products. Respectively starting from the left Seedling by TÜV Austria Belgium, German certifier DIN CERTCO, Vinçotte and CIC (logos).

The compostability of products that contain multiple materials (including additives) is recognized when all the conditions are met:

- All the materials in the product must be compostable, unless they can be easily separated (yogurt jar and its lid)
- Thickness of the product must be less of the total at which it has been tested and recognized that it biodegrades

- The product must not contain any additives harmful to environment or can worsen the quality of the compost
- The use of product must be specified in detail.

The schemes of certification are specified for industrial and home composting.
INDUSTRIAL label is guaranteed as biodegradable in an industrial composting plant (including inks and additives) at temperatures between 55-60°C for a maximum of 6 months.
HOME label guarantees complete biodegradability in the light of specific requirements at lower temperatures (between 20-30°C) and for a longer timeframe (maximum 12 months). This process is more difficult than the industrial due to the smaller volume of waste and the less constant temperatures.

Figure 2.6- Certification marks for HOME composting from DIN CERTCO and Vinçotte

What is "Biodegradable"
The term derives from the biodegradation process. This is the chemical process during which biological action degrades materials into water, carbon dioxide, methane, and compost. The process strongly depends on the surrounding environmental conditions (temperature, location) and timescale. Environmental parameters can be physico-chemical (temperature, humidity, pH) and micro-biological (quantity and nature of microorganisms). A product's application determines the ideal biodegradation environment.
It is important to not confuse the term biodegradable with compostable. Both terms are referred to product's characteristic to return to the nature once materials break down. However, compostable materials go one step further by providing the earth with nutrients (humus) at the end of controlled process. So, while all compostable material is biodegradable, not all biodegradable material is compostable.

Standards and methods

ASTM D5338[20] provides test methods for the determination of plastics aerobic biodegradation under controlled composting conditions, incorporating thermophilic temperatures. The biodegradability is defined as the ability of material to be converted into CO_2 thanks to microorganisms.

EN ISO 14855[21] is a standard biodegradation test method that determines ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions.

With ultimate aerobic biodegradation means microorganisms fully consume a chemical compound or organic matter by in the presence of oxygen. Produces carbon dioxide, water, and mineral salts. Test requirements for ISO 14855 are the same used for compostability. Biodegradation results require analysis of evolved CO_2 from a minimum of 90 days test.

A limitation seen with both ISO 14855 and ASTM D5338 is that these standard methods represent idealized composting facilities. To cover small-scale pilot composting, the ISO 16929 method is recommended in addition to the other standard test methods.

Certifications

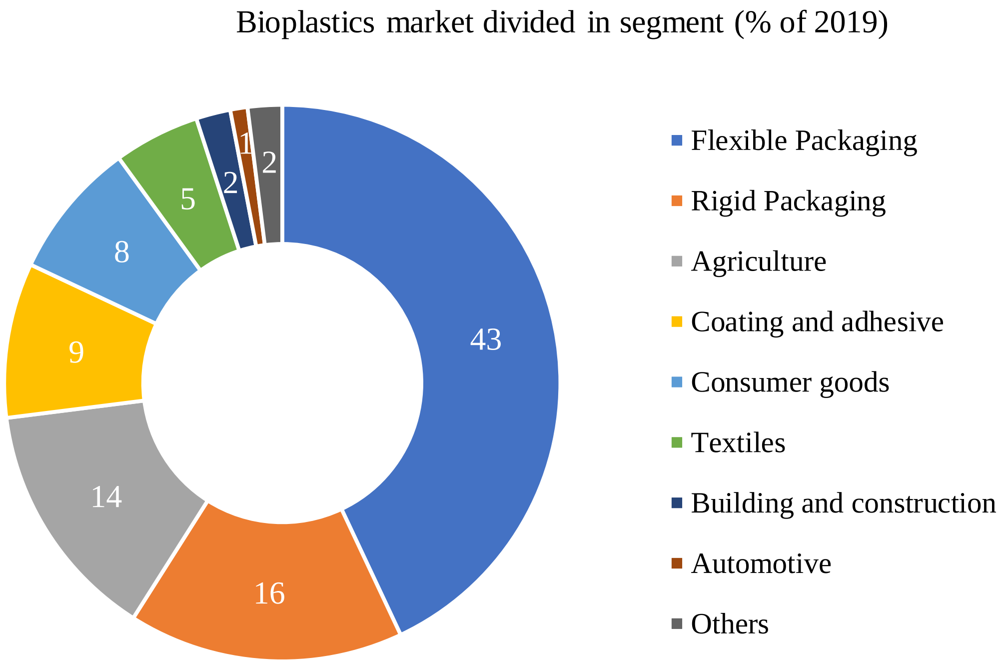
VINÇOTTE specifies the correct biodegradation environment for products declared as Biodegradable. The certification divides soil and water environment. The declaration guarantees that a product will completely biodegrade without negative impacts. It should also be noted that the certificate of biodegradability in water does not ensure that the product biodegrades in a marine environment too (i.e. in the presence of salty water).

Figure 2.7- Certification marks for Biodegradation in Soil and Water (Source: Vinçotte website)

2.2. Bioplastics in the market

In the recent years Bioplastics' market has potentially expanded. As the innovation and researches are going further, the demand for newer and diversifying biomaterials is rising. According to the latest market data report given by European Bioplastics, global bioplastic production is set to increase from 2.11 million tonnes in 2019 to 2.43 million tonnes in 2024. The dynamic growth is predicted to increase by more than 15% over the next five years. As for plastic, the largest demand is covered by Packaging sector; innovation aims to substituted ever more conventional disposable items. Almost 53% (1.14 million tonnes) of the total volume is destined for packaging market.

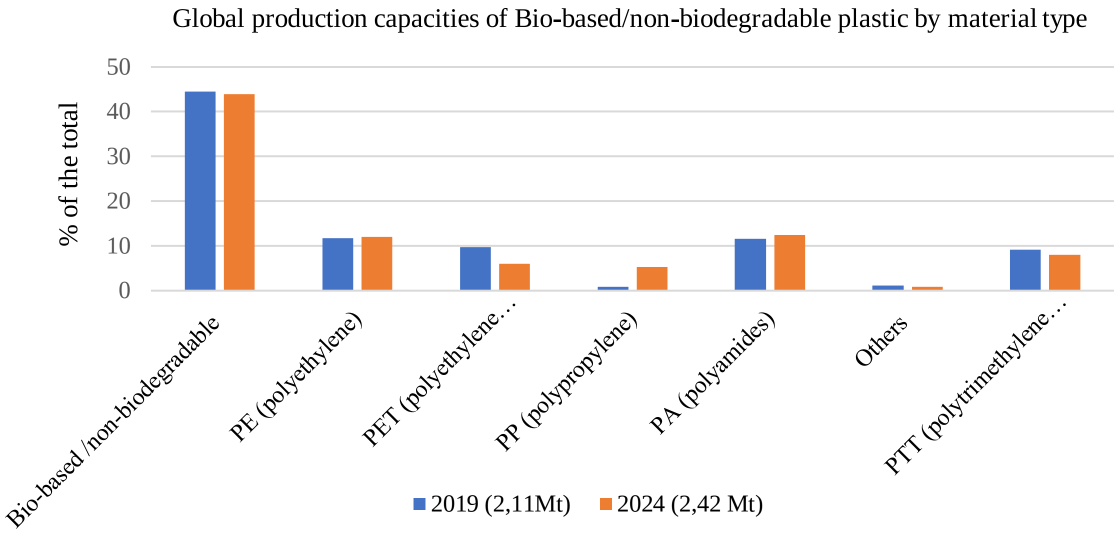
The land used to grow renewable feedstock for production of bioplastics can be a concerning problem. However, it is demonstrated that the actual disposition used (0.79 million hectares) covers only 0.016% of total global agricultural area of 4.8 billion hectares. Despite the market growth, the land use for bioplastics will slightly increase reaching 0.21% in 2024. This indicates that there is no competition between the renewable feedstock for food and feed and the production of bioplastics.

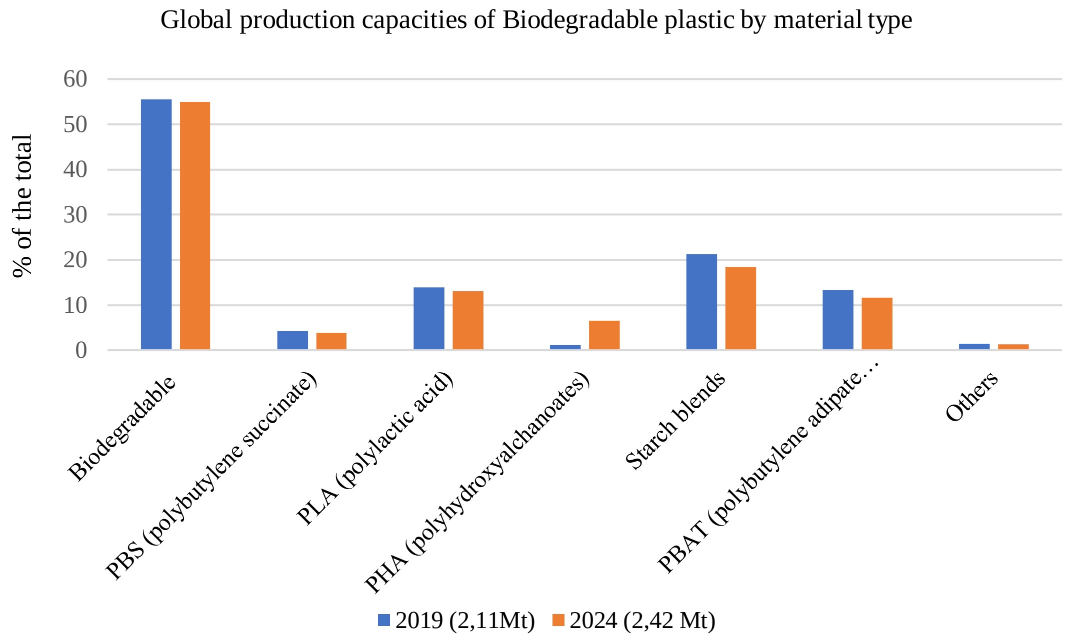


Graph 2.3- Bioplastic market segmentation in a total of 2.11 Mt of plastic demand for the year 2019

For almost every plastic material and application there is a bioplastic alternative which tries to substitute the properties and potential. As in conventional plastic market, PP (polypropylene) drives the demand, PHAs (polyhydroxyalkanoates) are leading the bioplastic one. Since more bioplastic materials will be available in the next five years, the production capacities will lightly change.

The production of Biodegradable material covered 2.11 Mt in 2019. The 2024's prevision forecasts a production of 2.42 Mt. The graphs 2.4 below compare the trends for both Bio-based/non-biodegradable materials and Biodegradable ones in years 2019/2024[22].





Graphs 2.4- Future global production trends for both bio-based/non-biodegradable materials and biodegradable ones considering years range 2019/2024. The division is done according to typology of material considered.

Most common biodegradable bioplastic in the market

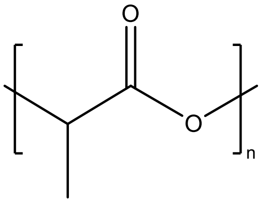
Table 2.1- Common Biodegradable plastics in the current market

Origin/End of life	Taken from Biomass (bio sourced)	From petroleum (not biosourced)
Biodegradable	TPS (thermoplastic Starch) PHA (polyhydroxy-alcanoates) PLA (polylactic acid) Bio-PBS (polybutylene succinate)	PCL (polycaprolactone) PBS (polybutylene succinate)

Polylactic acid (PLA)

Polylactic acid is a biodegradable thermoplastic polyester made up of lactic acid building blocks. By using lactide as raw material, PLA is considered bio sourced. Lactic acid can be produced by bacterial fermentation of a carbohydrate source under controlled conditions. However, in industrial scale, production of lactic acid can be corn, starch, cassava roots, sugarcane (first bioplastic generation).

There are two methods for manufacturing PLA: polymerization and condensation. The first technique consists in the direct polymerization of lactic acid to create a larger and high-density PLA molecule. The lactic acid is heated in the presence of an acid catalysts (metal) to form cyclic lactide. The condensation process is similar with the difference in temperature. Since the reaction tents quickly to equilibrium, this way produces a low weight molecular polymer (low density PLA).



Polylactic acid
$(C_5H_8O_5)n$

Figure 2.8- Chemical structure of Polylactic acid (PLA)

Advantages

PLA is bio-based and biodegradable. The major advantage is its nature and sustainable process by which is made, making it environmentally friendly choice of plastic. PLA is thermoplastic, meaning that will turn into a liquid in its melting point of 150-170°C. Thermoplastic quality allows PLA to be melted and reshaped without significantly degrading its mechanical properties. This makes PLA a desirable material for all types of recycling. In case of incineration, PLA does not release toxic fumes known as VOCs (Volatile Organic Compounds).

Disadvantages

Disadvantages in using PLA are linked to its high rigidity and therefore, fragility. However, blends with additive can improve flexibility. The biggest problem of PLA reserves is the slow decomposition outside of controlled environment. Even if PLA is biodegradable, it only be decomposed within three months under specific conditions (high temperature and rich microorganism presence). Naturally, in soil PLA is not biodegradable.

Thermochemical Properties

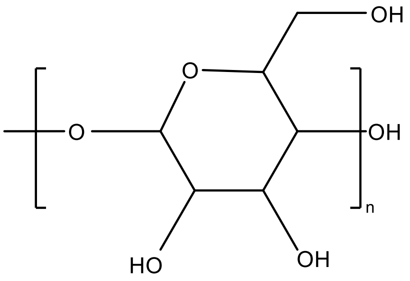
PLA has structure that varies according to process of synthesis: amorphous with glass transition temperature between 50-60°C, and semi-crystalline with a melting temperature between 130-180°C. However, PLA heat-resistant stands around 90°C, above which PLA degrades rapidly. For this reason, PLA is not suitable to hold hot liquids. The low softening temperature of PLA also creates problems for the storage of products and application in automotive industry.

PROPERTIES	APPLICATIONS	TRANSFORMATION
• 100% biobased • Biodegradable and industrially compostable • Rigid and fragile • Good barrier properties (oils,fats)	• Rigid and flexible packaging: containers, pots, bottles • Regular consumption goods • Non-woven or textile fibre • 3D printing	• Injection moulding and bowling • Thermofoming • Flat extrusion die or cast • Extrusion

Table 2.2- Summary of the main properties, applications and transformations of PLA

Starch and thermoplastic starch (TPS)

Starch is a totally biodegradable polysaccharide since it is synthetized by numerous plants during photosynthesis. Thanks to its abundance in nature, approximately 50% of the bioplastics are prepared from starch. In its granular shape, starch is mostly composed of linear amylose and highly branched amylopectin. The ratio of amylose and amylopectin varies with the botanical origin. Amylopectin is mainly responsible for the crystallinity of the granules. When mixed with little amount of water, subjected to thermomechanical forces, and added plasticizers, starch undergoes spontaneous destructurization. The “de-structured” is referred to physically modification of state, which results in the loss of order and crystallinity. The process leads to thermoplastic starch known as TPS.



Starch
$(C_6H_{10}O_5)n$

Figure 2.9- Chemical structure of Starch

Advantages

Starch is one of the most promising natural polymers because of its inherent biodegradability, availability, and annual renewability. Starch is very attractive for its competitive cost and ability to be processed with conventional processing equipment. The family of starches is very wide, and characteristics can vary according to different native feedstock (potato, corn, rice, cassava).

Disadvantages

The well recognized weakness of starch is its moisture sensitivity. In order to decrease the moisture sensitivity and increase mechanical properties, various blends are developed. Mostly synthetic polymers are used in blends. Consequently, the biggest drawback is the progressive loss in terms of biodegradability. Starch suffers thermal degradation.

Thermochemical properties

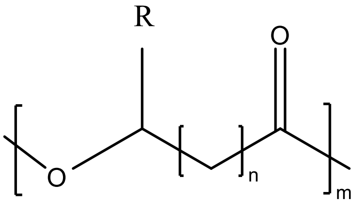
Starch belongs to carbohydrate organic compounds. The long chain is formed by condensation of glucose units. The strong intermolecular connection gives to starch hydrophilic properties. The use of starch alone is not encouraged because of its lack of melt-processability and humidity resistance. However, transformation in TPS, enhances mechanical strength, water solubility and absorption letting to an amplification in uses. The thermoplastification of starch entails the collapse of its crystallinity (general about 15-45% of the granule molecular order). By adding natural plasticizers as glycerol or sorbitol TPS enjoys more mobility.

PROPERTIES	APPLICATIONS	TRANSFORMATION
• 100% biobased • Biodegradable and compostable • Flexibile and brittle • Low cost • Great compatibility with sythetic and natural polymers	• Bags and trash bags • Short term consumable articles • Food packaging • Pharmaceutical packaging • Toys	• Processed with the existing plastic processing industry • Blow and flat film extrusion • Injection moulding • Therforming

Table 2.3- Summary of the main properties, applications and transformations of Starch

Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are a family of bio polyesters obtained by a broad variety of microorganism via fermentation of sugars and lipids. The organisms consume PHAs as energy sources. PHAs are biodegradable, compostable polymers. The wide family includes more than 150 types of PHAs that differ in homopolymers, copolymers and origin according to use of various bacterial species and growth conditions. The main division is due to length of chains (3-4 C atoms or more than 14). PHA's production methods include vitro and vivo. The first technique has the advantage to produce pure polymers, however it is low stable and expensive process. Currently this route is used for research. Production in vivo can be done in two ways: fermentation, used in industrial scale and through genetically modified plants.



Poly(hydroxylkanoates)

Figure 2.10- Chemical structure of Polyhydroxyalkanoates (PHAs)

Advantages

PHAs have better barrier properties and mechanical strength than other bioplastics. PHAs are stable to UV radiation thanks high light barrier. This quality is reflected as well in low permeability to water and vapours which allow a great resistance to humidity. Barrier properties are reflected in their quality to limit the loss of aromas and flavours made PHAs suitable in food packaging.

Drawbacks

Several drawbacks are limiting PHAs' propagation in the market. These disadvantages include their high production costs, limited functionality, and susceptibility to thermal degradation. Investigations must be undertaken to modify the high production cost (7-10 Euro/Kg). Possible solutions can be the utilization of substrates for bacteria growth which coming from waste materials and promoting the use of modified organisms in culture.

Thermochemical properties

PHAs are divided in short chain and long chain groups. Short chain are typically thermoplastics polymers so they can be processed up to melting point, approximately 180°C. They exhibit crystallinity between 60-80% and related disadvantages including their high fragility. Their melting temperature is close to degradation (200 ° C) and limits working range. However, the solution is the addition of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) copolymer to the chain. PHAs with longer chain are amorphous with a glass temperature between -62 and -26 °C. The melting temperature is very low varying from 42 to 58°C and lead to classify them as elastomers.

PROPERTIES	APPLICATIONS	TRANSFORMATION
• 100% biobased • Biodegradable and compostable • Duttile and elastic • Good barrier properties (light, aromas, oils and fats) • Low permeability to water	• Food packaging • Biomedical • Electrical and automotive sectors • Suitable for liquids • Films, sheets, fibers, non-woven products	• Thermoforming • Injection moulding • Extrusion is complicated but possible by using additives

Table 2.4- Summary of the main properties, applications and transformations of PHAs

Polybutylene succinate (PBS)

PBS is a biodegradable, semi-crystalline thermoplastic polyester synthesized through polycondensation of succinic acid and 1-4-butanediol. Both building blocks can be produced either from renewable feedstock such as glucose and sucrose via fermentation or from petroleum-based feedstock. PBS is commonly prepared via esterification or transesterification of succinic acid. Currently, succinic acid is produced from fossil resources through maleic acid hydrogenation. However, many industries start to produce succinic acid through fermentation of sugars. In this case, PBS turns the name in BioPBS.

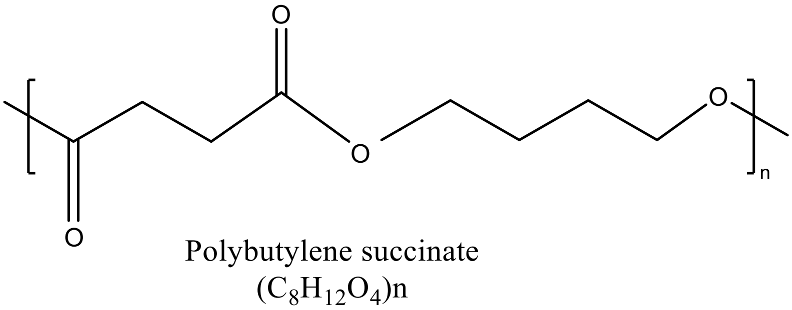


Figure 2.11- Chemical structure of Polybutylene succinate (PBS)

Advantages

Behind faster biodegradability than other bioplastics, PBS it is ambient compostable. The major advantage of PBS and BioPBS is their high compatibility with large number of biopolymers. Blends with natural fibres and fillers show great improvements in properties without the addition of any other products. Its mechanical properties are between those of conventional plastics PE and PP.

Disadvantages

PBS is one of the newest materials and could be a cost-effective alternative to other biopolymers. However, the disadvantage is the still limited use.

Thermochemical properties

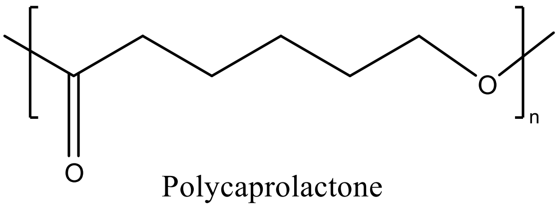
PBS has highly crystalline structure which gives it thermal stability from 90°C to 120°C. It exhibits multiple melting behaviour above 132°C. During processing at elevated temperatures PBS is sensitive to hydrolysis and needs to be dried prior use. PBS has high heat resistance with maximum processing temperature around 200-230°C.

PROPERTIES	APPLICATIONS	TRANSFORMATION
• Biodegradable and compostable • Flexible • Thermostable • Great compatibility with other biopolymers, natural fibres and fillers	• Food packaging • Compost bag • Suitable for hot liquids and oils	• Extrusion • Injection moulding • Thermoforming • Films • Foaming

Table 2.5- Summary of the main properties, applications and transformations of PBS

Polycaprolactone (PCL)

Polycaprolactone is biodegradable polymer from fossil origin. The synthetic chemical formation is the union of sequences of methylene which including ester groups. It has very high molecular weight. Due to the uniform structure it is readily crystallized. PCL is miscible and blends well with other plastics, as well as lignin and starch. PCL is often added for improving moisture resistance in biopolymers, increased melt strength and flexibility. PCL's preparation is simpler than other biopolymers.



Polycaprolactone
$(C_6H_{10}O_2)n$

Figure 2.12- Chemical structure of Polycaprolactone (PCL)

Advantages

PCL is biodegradable, biocompatible and bio assimilated. Low bioactivity is due to high hydrophobicity of the molecules. It shows good adhesion to a wide variety of substrates. It is easily pigmented and printable. Thanks to its low cost of processability, it has multiple applications. The PCL is used as an additive for other polymers and thanks to low melting point, can be moulded by hand. It is useful in prototyping and repairs plastic parts. Recently, it has received attention for use in biomedical application.

Disadvantages

PCL low melting point can be a limit in some applications. However high permeability to vapours, water, oxygen, and CO_2 remain great disadvantages. PCL is not compostable.

Thermochemical properties

Thanks to its simple structure, PCL has slightly limited rotation of the chain, leading to a very low glass transition temperature (-60 ° C). It is a semi-crystalline polymer with a melting point of 58-60 °C which limit the applications. PCL has low viscosity and high fluidity.

PROPERTIES	APPLICATIONS	TRANSFORMATION
• Biodegradable and bio-assimilable • Flexible • Hydrophobic • Great compatibility • Resistence to oils and fats	• Medical items • Films • Production of polyurethanes • Additive	• Extrusion • Injection moulding • Thermoforming • Films

Table 2.6- Summary of the main properties, applications and transformations of PCL

3. OBJECTIVE AND GENERAL CONTEXT

The thesis is part of a research project entitled *BECOMING GREEN* (Ref. IMDEEA/2019/68), financed by IVACE, Valencian Institute of Business Competitiveness of Valencian's Generalities, 50% co-financed through the FEDER Operational Program of the Valencian Community 2014-2020. The project aim is: "Development and improvement of biomaterials for single-use consumer products".

Figure 3.1- *BECOMING GREEN's* logo

Becoming Green's challenge is finding more sustainable alternatives to plastics, while maintaining the characteristics and functionalities of conventional ones. After 18 months of research the work seeks on offering to sectors as packaging, toy and household-goods, biodegradable materials for their use. Recently, the interest of companies in using bioplastics as substitutes for the manufacture of their products has increased considerably, either due to future legislative requirements or to customer demand. However, bioplastic still do not reach all the benefits offered by the traditional plastic. Therefore, depending on applications and requirement it is possible that plastic cannot be replaced in all cases. The biodegradable materials are suitable for processing with different conventional transformations (injection moulding, extrusion, thermoforming), although there are still lot of limitations in use. Nowadays, the companies which have incorporated biodegradable materials in their production process have met as main limitation the impossibility to satisfy the currently requirements on quality and safety. The problems are caused by poor resistance of biomaterials to high temperatures (70-80 °C), difficulties in heat sealing of the containers, fragility of the pieces due to high rigidity of the biomaterials and low barrier properties. Therefore, *BECOMING GREEN* addresses the attention at improvement of biodegradable polymers performance by testing their properties, to adapt them to quality and safety rules. So, the goal has developed around three main areas:

- Improvement of mechanical characteristics: reduction of the fragility of biodegradable materials
- Increased thermal stability in order to expand applications areas

- Enhancement of barrier properties

The exploitation of the results will be carried out by the application of improved bioplastics materials to target products. If the results are competitive in the market, the new formulations will be patented. Thanks to patent, the production of materials can be start generating products in large-scale process.

Basically, the working structure can be divided in levels. At the beginning, the exploitation in the laboratory is carried out with additional investigation in research, as attested in current European regulations. If the improved bioplastics show great results should substitute the target products. Once pass the first procedure, the new formulations could be patented. The patent gives the opportunity to starting large-scale production. In this way, it is desirable that market demand translates by replacing traditional fossil materials with biodegradable ones.

The entire project is focused on testing different biomaterials’ properties. The analysis use as bioplastics samples: polylactic acid (PLA), polyhydroxyalkanoate (PHA), thermoplastic starch (TPS), bio-polybutylene succinate (Bio-PBS) and polycaprolactone (PCL). Analysing the characteristics of the different biodegradable and biobased materials on the market, leads to evaluate the strengths and weaknesses comparing to conventional plastics. The classification of individual biomaterials was done according to their mechanical, thermal properties and suitable transformation process. In this way, it has been elaborated and reasoned on results in order to plan the next work’s activities. The wide initial possibility of experimentation in the laboratories, allowed to divide thesis work in two main parts and different specific objectives.

The first part is focused on analysis of compatibility between bioplastics. Binary mixtures were performed, in different percentages from a minimum of 20 to a maximum of 80%. The quantities 20% and 40% of Bio-Polybutylene succinate (BioPBS) blended with other bioplastics were selected for analysing mechanical properties. Characterization took place through the creation of standard samples obtained through injection moulding process.

1. *Compatibility of biopolymers in various percentages analysed through DSC, TGA. Further investigations include hardness and density for specimens prepared with compression moulding machine.*
2. *Improvement of mechanical properties of biopolymers’ blends, with an increasing quantity of BioPBS in ratio 80-20% and 60-40%.*

The second part is dedicated to experimentation on Polylactic acid (PLA). Among all biodegradable materials, PLA is deepen studied for its promising qualities. However, despite being attractive, some limitations can be improved. Researches aim to develop and optimize formulations to meet the market requirements and enhancing fracture resistance by adding more flexible polymers or additive. Formulations have been prepared by mixing PLA with an additive (VINNEX®). This addition aims to study enhancements in elasticity, reducing rigidity. The quantities of additive ranging from 5 to 20%. Moreover, a final comparison was made between mixtures of biopolymers, previous analysed, in percentage 60-40% with and without incorporation of additive (VINNEX®).

3. *Development and improvement of mechanical properties and complementary thermal analysis of PLA with percentages of VINNEX® ranging from 5 to 20% through injected samples.*
4. *Comparison between biopolymers' blends with and without addition of 10% VINNEX® 2504.*

The thesis project was prepared in the research laboratories of MATERIALS area in AIJU.

3.1. AIJU - Technological Institute for children’s products and leisure

Figure 3.2- AIJU’s logo

The whole *BECOMING GREEN* project is developed in AIJU (Asociación de Investigación de la Industria del Juguete, conexas y afines), in cooperation with toy and packaging companies of the Valencian Community.

AIJU is a Technological Institute which promotes innovation and knowledge in children’s and leisure products for companies and organisations. AIJU is a private, non-profit making centre aiming to boost research, development and technology that gives solutions to industry at both national and international level. The headquarter is in Ibi, Alicante (Spain).

The workers are part of a multidisciplinary team, mainly consists in industrial engineers, laboratory process technicians, chemists, and designers. Highly qualifies employees generate a know-how great confidence to the customers. Additionally, AIJU’s R&D Studies and Projects department have several lines of research. These are framed within the development of new models, materials, and technologies for the development of highly functional products with great added value. The activities within Areas are well related thanks to the good communication and collaboration network. The work is carried out in safety and advanced conditions, enjoying laboratories and pilot plants equipped with the latest technology available. All the activities are performing in the comply with the European legislation and current standards, which assure the validity of processes and data. These working’s methods make AIJU the only Technological centre of reference in Europe for R&D&I (Research, Development, Innovation) in children’s product and safety.

Why Toy sector

AIJU has a role of relevance and its competence is confirmed by awards won in toy sector. The European toy industry is one of the most important in the global international market. In Spain, there are 386 toy manufacturing companies, which 70% are located in Valencian Community[23]. As part of *BECOMING GREEN*, AIJU studied the possibility of incorporating biodegradable materials into the manufacture of toys and other consumer products by injection moulding process. Developments of these requirements are market oriented. The trends are moving towards the research for “green” materials.

Attention to a safe and sustainable future for children it also goes through the commitment in developing new materials that pose no risks and waste to future generations and environment. Technological developments in the world of toys have raised questions in relation to their safety in order to guarantee health conditions to children. Companies must update constantly legislation requirements at both regional, national, and European level according to changes in consumer trends and needs. It has recently been issued very stringent legislation by the European Community on safety of toys with Directive 2009/48/CE[24] commonly known with acronym TDS (Toy Safety Directive). The essential requirement is to not put chemicals in products that can present adverse reactions to people. It is expected that toys must be safe for both direct users and third parties. It is not enough that toys are safe only when they come used in the manner intended by the manufacturer, but they have to be in all the other possible ways and situations. *BECOMING GREEN* platform provides an exchange of information and knowledge by coordinating objectives in order to implement in even shorter time, researches and development. On the front line, *BECOMING GREEN* aims to demonstrate that it is possible to create new specific formulations with eco-sustainable and biodegradable qualities without sacrificing functionality and aesthetics of the final product.

4. MATERIALS

In this study, bioplastics were used, directly supplied from the financial Regional Found allocated for *BECOMING GREEN* project. The materials are produced from different international production companies. All the characteristics mentioned below, show data from the technical sheets of each materials.

Polylactic acid (PLA) – Ercros Bio® 652

The Spanish Ercros company, has developed a new line of bioplastics, which are marked under ErcrosBio® brand. PLA can exist in three possible isomeric forms, according to reaction in term of polymerization process: the poly (L-lactic acid) and the poly (D-lactic acid) are both semi-crystalline in nature, instead of the poly (D, L- lactic acid) it is amorphous. ErcrosBio® LL652 is a thermoplastic PLA obtained from natural and renewable materials. The total content of biological origin material is up to 99%. The crystallization rate increases with high mould temperatures (90 to 110°C). ErcrosBio® LL652 must be dried in a dehumidifier before processing. In fact, during the storage process it can acquire moisture depending on temperature, humidity, and time of exposition. It is specifically designed for injection moulding process with a temperature profile from 180 to 220°C. It is important to not exceed this temperature in order to avoid the possible degradation. ErcrosBio® LL652 is classified as no dangerous product according to European Regulation 1272/2008 and REACH declares the material as polymer in the obligations register. It is completely compostable according to criteria of EN 13432[19] standard, both at home and industrial levels. However, ErcrosBio® LL652 is suitable as well for mechanical (recovery as PET, due to similar properties), chemical recycling (recovery as acid lactic) and incineration. The products obtained with ErcrosBio® LL652 must be identified with code 7 "Others" for recycling.

PROPERTY[2]	VALUE	UNIT	METHOD
Technical name	**Polylactic Acid (PLA)**		
Melting temperature	180	°C	ISO 11357
Glass Transition Temperature	61	°C	ISO 11357
Young Module	3	GPa	EN ISO 527
Elongation at break	5	%	EN ISO 527
Maximum effort to traction	72	N/mm^2	EN ISO 527

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[2] Properties measured on injected samples. The properties of printed parts may differ from those measured on an injected sample.

Density	1.25	g/cm^3	UNI EN ISO 1183
Melt Flow Rate (MFI)	11	g/10 min at 195°C / 2.16 kg	ISO 1133-2

Table 4.1- Characteristics and properties of Ercros Bio® 652

Polyhydroxyaalkanoates (PHAs) - ErcrosBio® PH070

As for the PLA, the ErcrosBio® PH070 is a thermoplastic obtained from renewable natural materials. It has mechanical properties similar to the conventional LDPE (low-density polyethylene), barrier properties comparable to PET (polyethylene terephthalate) and soft feel, similar to PP (polypropylene) and LDPE. It is highly transparent, easily printable, and resistant to water-based products, fats and solvents. ErcrosBio® PH070 should be dried before use because may become moist if it is exposed too long to air. It is recommended to use a constant temperature profile of 160°C during injection moulding. The thermal degradation would lead to defects if exceeds 165°C. The product satisfies the Regulations, both EU and REACH. Moreover, ErcrosBio® PH070 is aerobically and anaerobically biodegradable and domestically and industrially compostable in accordance with the criteria of EN 13432 standard. It can undergo to recycling with code 7 and incineration process.

PROPERTY	VALUE	UNIT	METHOD
Technical name	**Polyhydroxyalkanoates (PHAs)**		
Melting temperature	143	°C	ISO 11357
Glass Transition Temperature	1	°C	ISO 11357
Young Module	1.7	GPa	EN ISO 527
Elongation at break	6	%	EN ISO 527
VICAT	100	°C	ISO 1133-5 Kg
Density	1.20	g/cm^3	ISO 1183-1
Melt Flow Index (MFI)	2	g/10 min at 160°C / 2.16 kg	ISO 1133-2

Figure 4.1- Characteristics and properties of ErcrosBio® PH070

Starch - Mater-Bi® EI51N0

MATER-BI is a family of biodegradable and compostable bioplastics obtained by pioneering technologies using starches, cellulose, vegetable oils and other combinations. Mater-Bi®

EI51N0 is a thermoplastic material, also named TPS (thermoplastic starch) produced by Novamont (Italy). It is particularly sensitive to moisture, for this reason it is recommend store material in a cool and dry warehouse, away from heat and light. The typical equipment for processing Mater-Bi® EI51N0 is injection moulding. The profile temperature suggested performing temperature from 140° to 210°C, bur can vary according to mould-machine complex. All grades of Mater-Bi are certified by qualified Bodies in accordance with the main European and international standards. Such certification guarantees the biodegradation in various disposal environments: industrial and domestic composting, biodegradation in soil according to EN13432.

PROPERTY	VALUE	UNIT	METHOD
Technical name	**Thermoplastic starch (TPS)**		
Melting temperature	167	°C	ASTM D3418
Tensile strength at break	39	MPa	ASTM D638
Young Module	2200	MPa	ASTM D638
Elongation at break	2.5	%	ASTM D638
Linear shrinkage	0.33	%	ASTM D955
Density	1.24	g/cm^3	ASTM D792
Melt Flow Index (MFI)	19	g/10 min at 190°C / 2.16 kg	ISO 1133-2

Table 4.2- Characteristics and properties of Mater-Bi® EI51N0

Polybutylene succinate (BioPBS) - BioPBS™

BioPBS™ is bio-based and biodegradable Polybutylene succinate (PBS) produced from polymerization of bio-based succinic acid. PTTMCC Biochem produce annualy 20.000 Tons of BioPBS™ in Thailand. The world's first and largest plant derived materials from natural resources such as sugarcane, cassava, and corn. BioPBS™ decomposes into biomass in ambient condition (30°C). Alike LDPE, BioPBS™ is soft and flexible semi-crystalline polyester with excellent properties suitable for extrusion. The recommended processing parameters include the pre-dried operation before using in order to prevent possible material quality deterioration. The material is suitable in current extrusion coating machine, blown film extruders and injection moulding machines. Since it has high heat sealability, it can be suitable to use with hot food and beverages up to 100°C. BioPBS™ has the same level of seal as conventional petro-plastic, so the same performance can be provide with less cost in waste disposal expense. Compounding BioPBS™ with other types of biopolymer can enhance each other to a greater degree of mechanical and thermal properties. BioPBS™ is fully biodegradable even at ambient temperature and compostable industrially and at home (EN 13432). Therefore, products can be disposed of along with organic waste.

PROPERTY	VALUE	UNIT	METHOD
Technical name	**Polybutylene succinate (BioPBS)**		
Melting temperature	115	°C	ISO 3146
Yield Stress	40	MPa	ISO 527-2
Stress at break	30	MPa	ISO 527-2
Strain at break	170	%	ISO 527-2
Flexural Modulus	630	MPa	ISO 178
Flexural Strength	40	MPa	ISO178
Density	1.26	g/cm^3	ISO1183
Melt Flow Index (MFI)	22	g/10 min at 190°C / 2.16 kg	ISO 1133-2

Table 4.3- Characteristics and properties of BioPBS™

Polycaprolactone (PCL) - Capa™ 6500

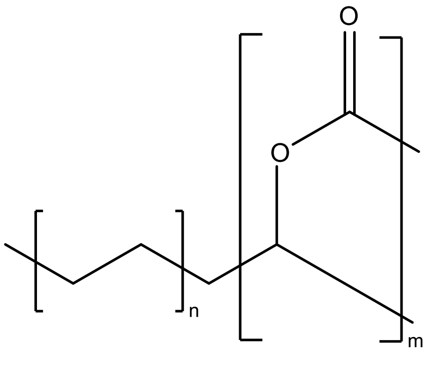
Capa™ 6500 is a thermoplastic linear polyester derived from caprolactone monomer. Capa™ thermoplastics typically are in form of granules (approximately 3 mm) that can be re-melted and re-moulded. Capa™ 6500 is used in a variety of adhesive applications and it is compatible with a wide range of common thermoplastics and soluble solvents. It is mostly performed for biodegradable packaging. General properties consist in high crystallization, high molecular weight, and high flexibility. On the other hand, low viscosity and low impurity in transformation process. Perstorp is the group which sells various families of Capa™ caprolactones. The mainly good performances for this type of materials are the easiness in processing, shaping and applications. They show outstanding flexibility even at low temperature.

PROPERTY	VALUE	UNIT	METHOD
Technical name	**Polycaprolactone (PCL)**		
Melting temperature	58-60	°C	ISO 3146
Water content	Max 0.35	%	
Elongation at break	800	%	
Solubility	9.34-9.43	cal/cm^3	ISO 527-2
Melt Flow Index (MFI)	7.90-5.90	g/10 min at 160°C / 2.16 kg	ISO 1133-2

Table 4.4- Characteristics and properties of Capa™ 6500

Additive - VINNEX® 2504

VINNEX® is Wacker's trade name for additives used as compatibilizer with biopolymers. VINNEX® are vinyl acetate-based homo, co or terpolymers additive. They are sold in powder, flakes, and beads according to what want to achieve. VINNEX® 2504 is a vinyl acetate /ethylene copolymer powder (VAc-E), beige in appearance and semi-rigid material. Typical application for this additive is referred to blends with natural fibres or flour such as wood, starch, and cork. It is highly recommended for the modification of biopolymers and their compounds. The temperature range in a thermoplastic process in a highly filled system is from 100°C to 150°C. Since VINNEX® 2504 can absorb humidity and it is sensitive to pressure, it must be stored in a cool and protected place.



Ethylene-vinyl acetate
$(C_2H_4)n(C_4H_6O_2)m$

Figure 4.2- Chemical structure of ethylene- vinyl acetate

PROPERTY	VALUE	UNIT	METHOD
Name	VAc-E		
Glass transition temperature	10	°C	
Bulk density	425-575	kg/m^3	DIN EN ISO 60
Ash content	6-9	%	
Density	1.27	kg/m^3	
Melt Flow Rate (MFI)	3.1	ccm/10 min at 150°C / 2.16 kg/2 mm	
Young modulus	0.63	MPa	DIN EN ISO 527 (200mm/min)
Elongation at break	326	%	DIN EN ISO 527
Tensile strenght	11.29	MPa	DIN EN ISO 527

Table 4.5- Characteristics and properties of VINNEX® 2504

5. EXPERIMENTAL METHODS

All the materials considered for the analysis are stored following the indication of technical sheets. The bags were correctly closed and put preferable in places away from light source and heat, in order to avoid humidity's penetration. For creating the blends of biopolymers, the materials were physically mixed. Once calculate the percentages of material needed for blending, the specific quantities were weighted with laboratory balances. All the instruments were correctly calibrated and complied the regulation. The materials and equipment used are suitable for laboratory test scale. It is important to establish the specifications relating to conditioning and tests. In fact, in order to compare the various results on materials it is necessary to standardize the humidity and temperature conditions to which the specimens are subjected before and during the tests. In this case, the atmospheric condition used, takes the name of "room temperature".

5.1. Samples fabrication process

Dehumidifiers

Since the amount of moisture can greatly affect polymers quality, accurate humidity content is important to measure before any operations. Dehumidifiers can accept different forms of samples (grain, powder, particles, liquid) single or in blends.

FD-720 Infrared Moisture Analyzer is used for little quantity. The method consists in weighting the sample while heating (drying-weight method). The weight loss reflects water loss and gives an information with high accuracy (0.1%). The heater source is a large 400 watts Midwave infrared quartz heater controlled by the software for drying process. There are 10 measurements conditions in instrument memory differing in temperature and time.

For each material analysed, the humidity value is represented in percentage (%). The temperature and duration of drying must be scrupulously selected according to the type of polymer. Too long duration or too high temperatures can cause phenomena of thermo-oxidative degradation. For this work, samples about 10 grams were putted between two aluminium dishes handlers. The condition 3 was selected, with a temperature of 50°C and time of 3 minutes. The humidity can vary from 0.2 to 0.5%. These percentages do not affect the quality of materials and allow the validity of next operations.

Dri-Air mini-dryer is designed to dehumidify more quantity of materials (around 5kg) with a longer process. Compared to Air *FD-720, Dri-Air mini-dryer* uses hot air to eliminate moisture out of the materials. Typically, mini dryers are designed to be compact and easy to use for extrusion, moulding at lab applications' scale. With the Control is possible setting the temperature of processing varying on the type of materials placed inside.

a) b)

Photo 5.1- a) FD-720 Infrared Moisture Analyzer; b) Dri-Air mini-dryer

For drying the extruded material, it has been decided to use a *Vacuum drying oven*. This passage was an additionally elimination of humidity residues that could be kept during the extrusion process.

Photo 5.2- Vacuum drying oven

Plastograph

The blends are made using the Plastograph, *Brabender* equipment. This machine is fundamental in mixing process, making components distribution more homogeneous. The binary blend of materials (approximately 40 grams) is loaded through a hopper in the mixing chamber. A weight above allows to press materials in the heated chamber. In this section the homogenization of materials takes place thanks to the rotation of twin-screw rotators.

The path of blend can be visualized and modified through *Win Mix* programme. With the software is possible to manage and change: temperature of the mixing chamber, duration of the process and control rotor speed. These variables could be modified according to the type of materials in use. The resulting diagram illustrates the relationship between torque (viscosity) and temperature over measuring time. Once the process is finished, the material is detached by cleaning, with jet of compressed air, rotators and the walls of the mixing chamber and stored in a collection container. The process is discontinuous, and a formless solid material is obtained.

Sample weight	40 grams
Rotators Speed	50 rpm
Process Duration	3 minutes

Photo 5.3- Brabender plastograph. **Figure 5.1-** Conditions settled in plastograph

Plastograph *Brabender* machine is used for mixing together materials. All the blends were processed in conditions show in the table 5.1. The variable temperature changes according to characteristics and types of materials.

Pelletizing

Photo 5.4- Pelletizing Moline machine

The industrial plastic crusher mill shreds pieces of materials. The mill is an intermediate passage instrument. The material crushed in this way allows its second use in other machines and instruments which need pellet shape. The mill consists of an inlet whose size allow the plastic parts enter. It has a rotor that incorporates a series of blades that crush the material. The material obtained at the end of the process fall in a collector through the exit perforation. The iron grill allows the passage of a certain size of piece or grain. The final pieces of materials have not a homogeneous shape and in case, they can be crush again until not reached the expected size.

Compression moulding machine

Compression moulding is a process in which an amount of thermoplastic or thermoset materials melt under specific temperature and pressure and take the shape of the mould. The material (granule or pellet), is placed inside a mould which rests on a metal sheet. The sample is closed between two metal sheets that prevent the leakage of materials. The mould is pressured between the two metal sheets by the preheated plates. Fundamental are the two heated plates, one fixed on the top and the other mobile, controlled by a system. The plates can be cooled by water and/or by a cooling system inside. Temperature, pressure, and time are the parameters which guide the entire process. These can be set manually by control panel outside the machine. The maximum eligible pressure on the sheets (20 x 20 cm sizes) is 200 bar. When the hot cycle is completed, the plates open and cooling cycle starts. When the cooling is completed, the two plates will be separated. The mould is ready to be removed from the machine. The two metal sheets which contain the mould sample can be cooled by air or water depending on material. The resulting specimens are not yet included in any standard regulations.

Photo 5.5- Compression Moulding machine

Extruder machine

Photo 5.6- Extrusion machine and process in the laboratory

The extrusion is one of the most decisive processes in transformation of thermoplastic materials. The extruder allows to obtain material quickly and continuously by operating with raw material, often in form of granules or powder. The extrusion machine works with thermoplastic granules by pressing, melting, moulding, pushing materials from a hopper through a die by a rotating screw.

The machine consists in:

- *Loading hopper* though which the extruder is fed with plastic granules. Its task is to convey the plastic pellet, by gravity, into the cylinder feeding section.
- *Rotating cylinder* has twin-screw (rotating in concordant or discordant direction). The purpose of the cylinder is to provide the development path to the material through the whole length. The movement of screw forces the material through the orifice called the die. Calculation of the screw diameter and length is based on the melting rate, size of the resin, type of raw plastic and amount of pressure required for maintaining uniformity. The twin screw's design may be used to enable adequate mixing.
- *Heating chamber* keeps the temperatures manually settled for each type of material.
- *Shaping Die* is the end of extruder barrel machine. The cross-section of the die determines the dimension and shape of the profile.
- *Cooling zones* is where the profile passes through a moving water bath and jets of compressed air, in order to remove heat from the profile.

- *Cutter* is the final part reached by the plastic profile where is pelletized or curled in a coil. To change the profile's diameter, the extrusion volume and cutting speed are automatically adjusted.

a) **b)**

Photo 5.7- Photo a) shows the shaping die, when materials previous melted comes out the extruder and started to be cooled in the water. Photo b) shows the cutter, a pelletizing machine where the profile after the passage become against pellet, to be used in the next operations.

Injection moulding machine

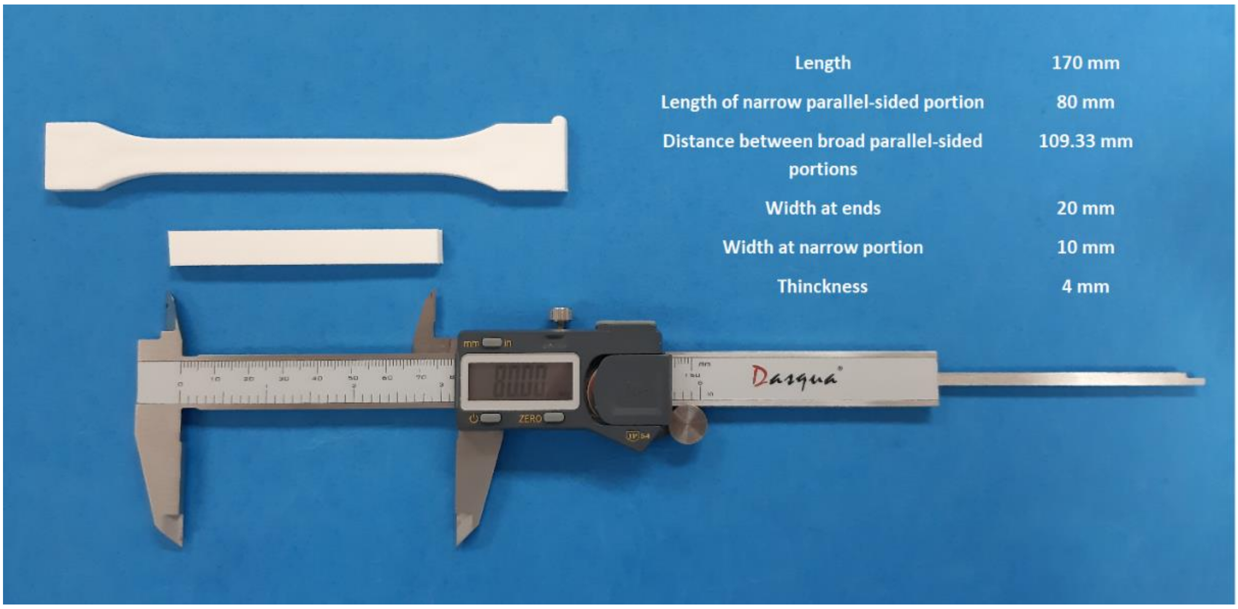
Photo 5.8- Injection moulding machine

Injection moulding machine is used for manufacturing plastic products by the injection moulding process. In this case, the process was used for the development of standardised samples which will be characterized according to standards. Basically, the manufacturing process consists in melting the materials and injecting it at high pressure into a mould. The material is cooled rapidly, solidified and it can release from the opening two mould halves. The technique results in a predetermined and fixed shape where the mould is divided into two halves. The process cycle for injection moulding varies according to material's characteristics but generally is very short. It consists in four stages:

- *Clamping*, before the injection, the two valves of the mould must be securely closed by the clamping unit.
- *Injection*, the material (granules or pellets) is fed into the machine and starting to melt by heat and pressure. The amount of material injected is referred to a shot that the mould can hold.
- *Cooling*, when materials is pushed inside the mould begins to cool quickly. It solidifies in the desired shape. The mould cannot be open until the required cooling time has elapsed.
- *Ejection*, when a sufficient time has passed, the cooled part of the mould can be ejected. When the mould is opened, an applied force, pushes the final products outside the machine. For this work, the conditions allow to use a silicon spray in order to facilitate the ejection of some materials.

The variables change according to the blend of materials injected. The parameters modified were profile temperature (°C), temperature of the mould, velocity (cm^3/s), time (s) and pressure (bar) of compactation, cooling time and loading speed (rmp).

International standard ISO 3167:2002[25] specifies requirements relating to multipurpose test specimens for plastic moulding materials intended for processing by injection or direct compression moulding. Specimens of type 1A are tensile test specimens from which all the test methods can be performed. The principal advantage of these test specimens is that allow multiple test methods. The properties measured are coherent as well as reproducible. The figure 5.9 below shows the injected 1A type specimen used in tests. The specimens are standardized samples cross-section. All specimen's surfaces must be free of visible defects, scratches, and imperfections. All existing burrs on the specimen must be removed.



Length	170 mm
Length of narrow parallel-sided portion	80 mm
Distance between broad parallel-sided portions	109.33 mm
Width at ends	20 mm
Width at narrow portion	10 mm
Thinckness	4 mm

Photo 5.9- 1A type of specimen used for tests in laboratory. Photo shows the standard dimensions

5.2. Techniques and characterization tests

Once the blends have been processed and the samples obtained, characterization follows. Specifically, each test corresponds to several references and standards. Three groups of characterization tests are carried out: mechanical, physical, and thermal tests.

5.2.1. Mechanical characterization

The mechanical characterization tests include: the tensile traction test, the flexural test, the impact test by Charpy method and the Shore D hardness.

Traction test

This test is carried out following the ISO 527-2:2012[26] standard: the determination of tensile properties for moulding and extrusion plastics. These properties include maximum resistance (MPa), percentage elongation at the yield point (%), Young's modulus (MPa). With this standard is required a specific moulded specimen type: 1A. The testing electromechanical machine *INSTRON 6025* by Zwick Roell allows to perform tensile tests at range of loads up to 100kN. Data are recorded and analysed through the programme *testXpert.* In the tensile test, the specimen is stretched along its longitudinal major axis at constant speed until it breaks or until the unit load of deformation (elongation) has reached a pre-determined value. The extremities of specimen are larger so they can be readily gripped by the machine, while the gauge area has smaller area where deformation and failure occur. For ISO 527 the test speed is typically 5 or 50 mm/min for measuring strength and elongation and 1 mm/min for measuring modulus. The extensometer is used to determine elongation and tensile modulus. The parameters provide information on both ductile and resistant behaviour of materials tested. To obtain reproducible values, the tensile test was carried out on at least five different specimens and the average value is calculated. The calculation of unit load value based on initial cross section of specimen is done following the equation:

$$\sigma = \frac{F}{A}$$

where:

σ: is the tensile unit load value, expressed in megapascal (MPa)

F: is the force in question, measured in newtons (N)

A: is the area of the initial cross section of the specimen test, expressed in square millimeters (mm^2)

Photo 5.10- *INSTRON 6025* by Zwick Roell machine used for both traction and flexural tests

Flexural test

The test follows ISO 178:2019[27] standard for determination of flexural properties. The standard is addressed to rigid and semi-rigid plastics under defined conditions. The equipment is the same used for traction test (*INSTRON 6025* by Zwick Roell). The method is used to investigate properties' specimen such as flexural strength, flexural modulus, and other aspects of stress/strain relationship. The test is performed on test specimen which has specific dimensions. The standard specifies two methods for calculating based on speed of deformation. The resulting curve of deformation depends on ductility of the material. The data are expressed in percentage (%). The calculation is based on length of specimens measured, using the following equation:

$$\mathcal{E} = \frac{\Delta L}{Lo} \quad \text{and} \quad \mathcal{E}\,(\%) = 100 \times \frac{\Delta L}{Lo}$$

Ɛ: is the deformation value, expressed as dimensionless ratio or a percentage

L0: is the length measured on the specimen expressed in millimeters (mm)

ΔL: is the increase in the length of specimens during the test, which is measured and marked in millimeters (mm)

While calculation of tensile modulus of elasticity is based on two specified strain values:

$$\text{Et} = \frac{\sigma 2 - \sigma 1}{\varepsilon 2 - \varepsilon 1}$$

Et: is the tensile modulus of elasticity expressed in megapascals (MPa)

$\sigma 1$: is the MPa stress measured at the deformation value $\varepsilon 1 = 0.0005$

$\sigma 2$: is the MPa stress measured at the deformation value $\varepsilon 2 = 0.0025$

Photo 5.11- Flexural test on specimens

Charpy test

This test is performed with *RESIL IMPACTOR* instruments according to ISO 179-1: 2010[28]. The equipment, ideal for quality control and research, uses a pendulum of 1 Joule or 5 Joule in energy. Charpy impact strength is defined for plastic materials with different types of specimens and type of notch. For this type of test, 1A type specimen were used without the heads (total length 80 mm). The method can be used to investigate the behaviour of specimens under the impact conditions defined, for estimating the brittleness or toughness of specimens within the limitations inherent in test conditions. At least 10 different specimens were tested, and the energy absorbed on impact (Charpy impact resistance) was calculated to the ratio of the absorbed energy to the cross-sectional area of the specimens. All Charpy impact test were performed at room temperature. The specimens can be carved or not according to the pendulum’s capacity to break them. For calculating Charpy’s results, specific specimen dimensions are requested.

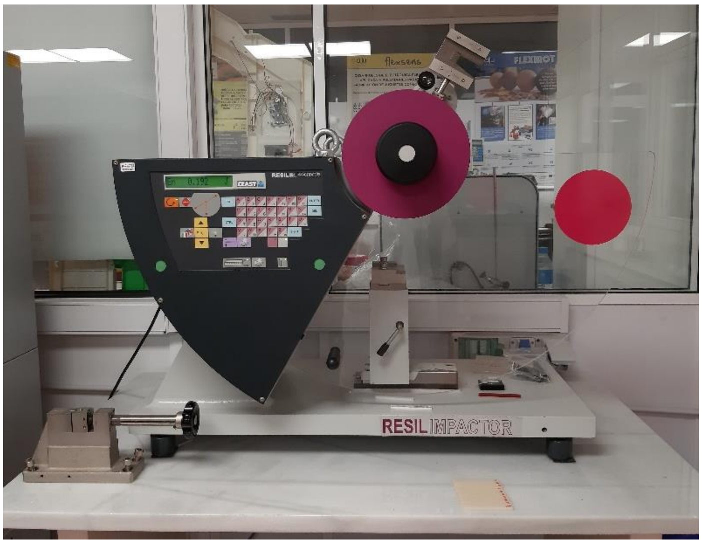


Photo 5.12- RESIL IMPACTOR for Charpy test with pendulum of 1 and 5 Joule

The *Notching Machine* enters in use, when Charpy equipment cannot read the result because of the incapacity of specimen to be broken. This manual machine is easy to use, the equipment ensures the clamping of specimen and then starts cutting it. The speed of cutting can be controlled. When the specimen is correctly placed, the machine cuts it exactly in the middle. Each manual turn of the wheel corresponds to a cut of 1 mm depth in the width of specimen. For the Charpy test, notch of approximately 2 mm in depth is required. The notch allows the specimen to be broken with a pendulum of less energy. Typically, with carved specimens a pendulum of 1 Joule is used. On the other hand, without carving the specimens a 5 Joule hammer is used.

After the cut in specimens, the dimensions are calculated. Even if the notch is approximately about 2 mm, it is important to be precise. For the calculation a *HE400 Horizontal Benchtop Optical Comparator* was used. The system consists in precision optics, light and highly accurate workstage which combine to ensure bright, sharp images and accuracy in calculations. The calculation has an error of 0.01 mm. Specimens' dimensions are marked and the Charpy test can follow.

a) b)

Photo 5.13- Photo a) shows the notching machine for notching specimens. Photo b) shows HE400 Horizontal Benchtop Optical Comparator for correctly measured the specimens.

Hardness test

This test is performed following the ISO 868:2003[29] standard using a durometer. The durometer scales can vary with the different materials properties. SHORE D scale is the scale used for harder materials. Durometer measures the depth of a hole in the material created by a given force on a standardized presser foot. Basically, the test requires applying constant force, without any shock and check then the value indicated. Measurements were carried out on five various parts of the specimen in order to obtain the average values with maximum reproducibility. This characterization was done at room temperature.

Photo 5.14- Manual durometer for calculation of hardness in SHORE D scale

5.2.2. Physical characterization

Density measurement defines physical characteristics of a material. Density is mass of material for volume unity. Its determination is an important qualitative parameter for both virgin and blends materials. The procedure is based on hydrostatic thrust technique using Archimedes principle. Density determination was done with *METTLER TOLEDO* analytical and precision balance (resolution of 1 mg). By converting the laboratory standard balance with the density determination kit, the performance is simple and fast. The instrument includes: a beaker of distilled water (standard density of 1 g/cm^3 around 21°C) where putting the sample; a thermometer for checking the liquid temperature and a balance for the both measures. First, the sample is weight in the air, once recorder the data, it is weighted again inside the liquid with standard density. The sample's density can be calculated automatically with the instrument. Each measure is done with a little quantity of material in pellet (from 0.5g to 1g). The result is the average of five repetitions for each sample. The unit considers is express in g/cm^3. All the tests were performed at room temperature.

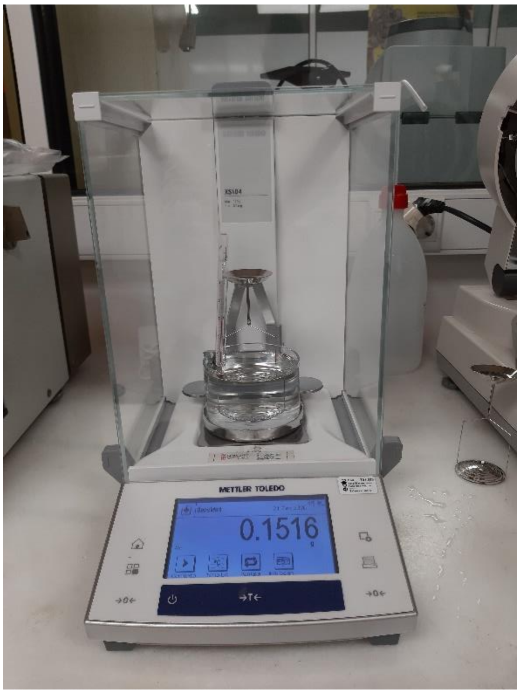


Photo 5.15- METTLER TOLEDO analytical and precision balance. The photo shows the measuring of density.

5.2.3. Thermal characterization

Three types off thermal characterization are contemplated in this section: Different scanning calorimetry (DSC), Thermogravimetry (TGA), Fourier-transform infrared spectroscopy (FTIR) and Flow index determination (MFI).

Different scanning calorimetry (DSC)

To obtain the most relevant thermal transitions of materials, a different scanning calorimeter *Q200* from *TA Instruments* was used (USA). ISO 11357-1[30] defines the standard method for the thermal analysis of both polymers and polymers' blends. DSC is a thermoanalytical technique used to investigate the response of polymers to heating. It is a technique according to which the difference between the thermal flow (power) entering the test sample and the reference test is measured as a function of temperature and/or time while these samples are subjected to specific temperatures. The sample undergoes a physical transformation according to changes in temperatures. The DSC set-up is composed of measurement chamber and a computer. The data are plotted in a diagram where temperature/time are in x axis and heat flow on the y axis. The resulting curve is obtained from three stages of the thermal cycle. The first heating cycle starts at room temperature (typically 30°C) to 200°c, the second consists in cooling stage from 5°C to -90°C and finally, a second heating stage of 10°C to 350°C. The heating/cooling rate is 10°C/min. Nitrogen gas is used to stabilize the sample during the performance of the analysis at a flow rate of 50 mL/min. The analysis was done with a sample previously weighted about 7-12 mg. The sample is putted in an aluminium pan, a second empty pan is used as a reference. The reference pan is a test sample recognized as generally inert in the field of temperatures and times considered. The rate of temperature change for a given amount of heat and differs between the two pans. This difference depends on the compositions of the pan contents as well as physical changes and phases changes of materials. The computer shows the result after 120 minutes.

Photo 5.16- Q200 equipment of TA Instruments

Thermogravimetry (TGA)

This test is performed using *TGA/SDTA* equipment supplied by *Mettler-Toledo* (USA). Thermogravimetric Analysis is a technique that consists in measuring the mass of a sample over time as the temperature changes. The analyser consists in a precision balance with a sample pan located inside a furnace with a programmable control temperature. The heating cycles start from room temperature. The first stage goes to 600°C, the second cycle to 1000°C. The thermal reaction occurs under ambient air atmosphere with a rate of 20°C/min. The analysis take in total 49 minutes. The thermogravimetric data collected from the analysis is a curve which plots the changes in mass over temperature or time.

Photo 5.17- TGA/SDTA equipment by Mettler-Toledo

Fourier-transform infrared spectroscopy (FTIR)

Infrared spectroscopy or IR spectroscopy is qualitative and complementary analysis to other identification techniques (DSC, TGA). The analysis was performed by using Thermo Scientific *NicoletTM 6700 FT-IR* spectrometer. Since each substance generates a characteristic spectrum, the aim of IR of Fourier (FT-IR) is to measure the absorption spectrum of a substance at different wavelengths. In this way, the easy and fast analysis allows the determination of the polymer class in the sample tested. The evaluation of new spectrum is done through the recognition of IR spectrum for some compounds already known. However, as the majority of materials examined are mostly new, the equipment does not recognize them. There is not yet a data bank for bioplastics materials. Therefore, data from this analysis were collected in the software but not effectively used.

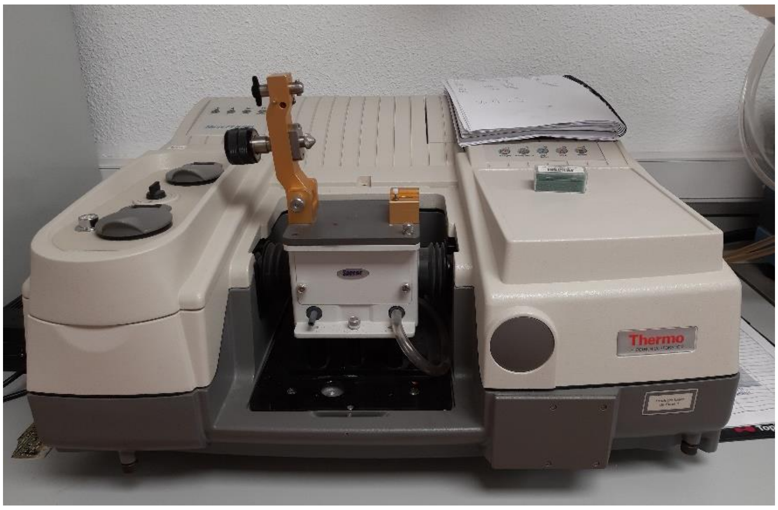


Photo 5.18- Thermo Scientific *NicoletTM 6700 FT-IR* spectrometer for infrared spectroscopy analysis

Flow index determination (MFI)

The determination of index flow is carried out to determine the influence of temperature on rheology of the virgin materials or blends. The test is performing according the ISO 1133-1:2012 [31] standard. MFI is defined as the mass of polymer, in grams, which flows in a set time of 10 minutes, through a capillary of a specific diameter and length at a given pressure and temperature. The pressure is given by standard weight of typically 2.16 kg, 5 kg or more. A small amount of sample is putted inside the apparatus and the flow profile is cut in a period of 15 seconds. The resulting samples are finally weighed, and data are averaged. MFI results are given in g/min. For calculated the MFI, it is important to use the equation below that considers the flowing mass of material with time.

Photo 5.19- Melt flow equipment

$$MFI = \frac{t_{ref} \cdot m}{t}$$

Tref = cut time (15 sec)

m = average of weights (g)

t= total time (10 minutes = 600 sec)

6. RESULTS AND DISCUSSION

6.1. Result 1

Compatibility of biopolymers in various percentages analysed through DSC, TGA. Further investigations include hardness and density for specimens prepared with compression moulding machine.

Mixing two or more different polymers is known as blending. Blending of polymers is widely studied for development and improvement of properties' material. In fact, the aim of blending is the production of new uniform material with range of properties different and better from those of the constituents. Blends of biopolymers are receiving importance in industrial applications due to their possible enhancements in mechanical and thermal characteristics, by decreasing costs. The compatibility of blends can be studied in terms of structure properties relationships. A property as the miscibility depends on the strong interactions between materials' structures. It is visualized through thermo-analysis particularly differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)[32]. After analysing virgin bioplastic, special interest was addressed in blends and in results' comparison.

Blending process

Blending is an efficient way in preparation of samples. Since the first passage is the feed of plastograph, the measures have been done according to capacity of machine (40g). Materials can be quantified into the blends by volume quantity expressed in percentages (volumetric blending) and by weight (gravimetric blending). Once decided the percentages which want to investigate, the materials were metered thanks to a laboratory balance with an error of 0.1 mg. Then, the bioplastics blends were manually mixed in beaker before being processed. This action promotes dispersive and distributive mixing.

Biopolymer 1 (%)	Biopolymer 2 (%)
100	-
80	20
60	40
40	60
20	80
-	100

Biopolymer 1 (g)	Biopolymer 2 (g)
40	-
32	8
24	16
16	24
8	32
-	40

Table 6.1- Tables illustrate the volume quantity express in percentage (%) and weight (g) respectively, used in biopolymers' blends

All the binary blends are performed in the same percentages and weight stated in table 6.2. Temperatures in process were chosen according to a series of information. First, following technical data provided by specific materials' sheets, secondly, results of virgin bioplastic from TGA analysis. In this way, it was possible to know the exact temperature at which the bioplastic starts melting (Melting Temperature, Tm). Combining both results, it was decided the temperature at which plastograph behaves better, to not degrade the materials.

Number of blends	Type of Blend	Temperature in Plastograph (°C)
1	PLA + PCL	200
2	PLA + PHA	195
3	PLA + TPS	200
4	PLA + PBS	200
5	PBS + TPS	190
6	PBS + PHA	160
7	PBS + PCL	150
8	PHA + TPS	190
9	TPS + PCL	190
10	PHA + PCL	160

Table 6.2- Processing temperature in plastograph for biopolymers' blends

Thermal characterization

After being pelletizing, all the blends are characterized by thermal analysis: DSC and TGA. The most important deriving data is the glass temperature. The glass transition phenomenon characterizes almost all single polymers. Glass transition temperature (Tg) corresponds to temperature when occurs transition from a partially rigid state (glassy) to a more malleable state (rubbery state). Tg value depends on the mobility of polymer chain and blends' structure. In general, a miscible polyblend exhibits a single glass transition temperature (Tg) intermediate between those of the constituent polymers. As for the virgin bioplastics, it was considered the Melting temperatures (Tm) in the second heating cycle during DSC analysis. According to the procedure, DSC curve is the tool adopted for the compatibility study.

From the resulting data, it is possible to notice that all blends of various materials, in different percentages do not show compatibility. This is conducible to the two distinct melting points in DSC results which coincide with Tm of virgin bioplastic.

Virgin Bioplastic material	2° heating cycle (°C) DSC	
	Tm	∆Hm(J/g)
PLA 652 Ercros (PLA)	174,68	13.62
PH070 Ercros (PHA)	142,65	35.11
CAPA 6500 (PCL)	57,48	71.78
Mater-Bi EI51N0 (TPS)	169,45	21.97
BioPBS (PBS)	114,17	73.67

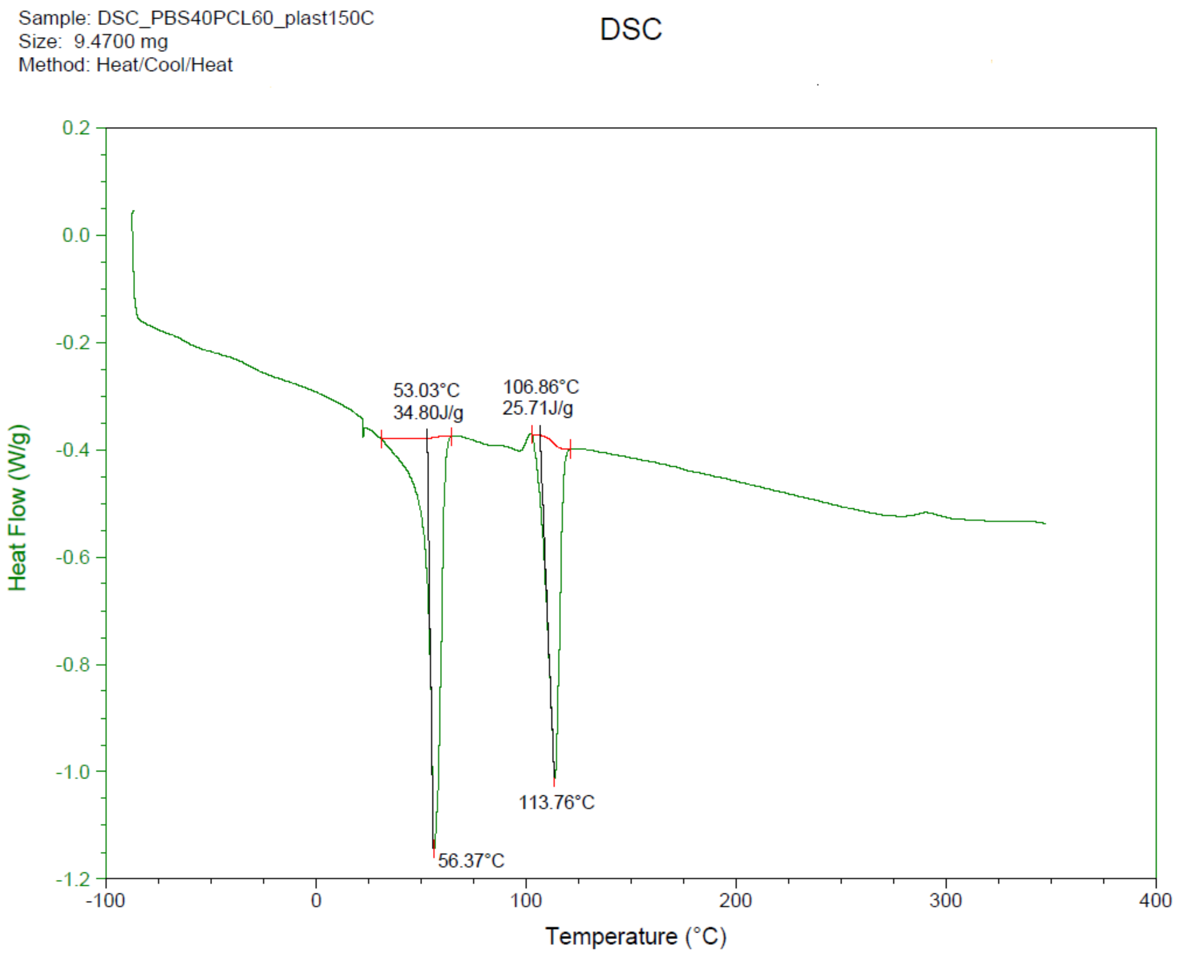
Table 6.3- Melting temperatures (Tm) and enthalpies (∆Hm) found with DSC analysis for virgin bioplastic

Results of DSC analysis in all single bioplastic materials. Table 6.3 shows the two parameters consider in the second heating cycle: Melting Temperature (Tm) and Enthalpy of melting (∆Hm). Tm is used to understand when change in phase occurs (exothermic reaction), the enthalpy can be used to measure crystallinity.

Processing temperature of plastograph 150°C	BioPBS/PCL	
	T_m PCL (°C)	T_m PBS (°C)
BioPBS100	-	114,22
BioPBS80	56,27	114,05
BioPBS60	56,51	114,04
BioPBS40	56,37	113,76
BioPBS20	56,82	113,43
BioPBS0	57,2	-

Table 6.4- Tm for biopolymer blend 7 (PBS/PCL)

Example of DSC analysis in blend BioPBS/PCL. It is visible that both Tm values coincide with that of virgin BioPBS and PCL. This is an evidence of incompatibility between the materials. In addition, the figure below shows the result of DSC analysis for the blend 40% BioPBS + 60% PCL. The two picks are further confirmation of the incompatibility between materials.

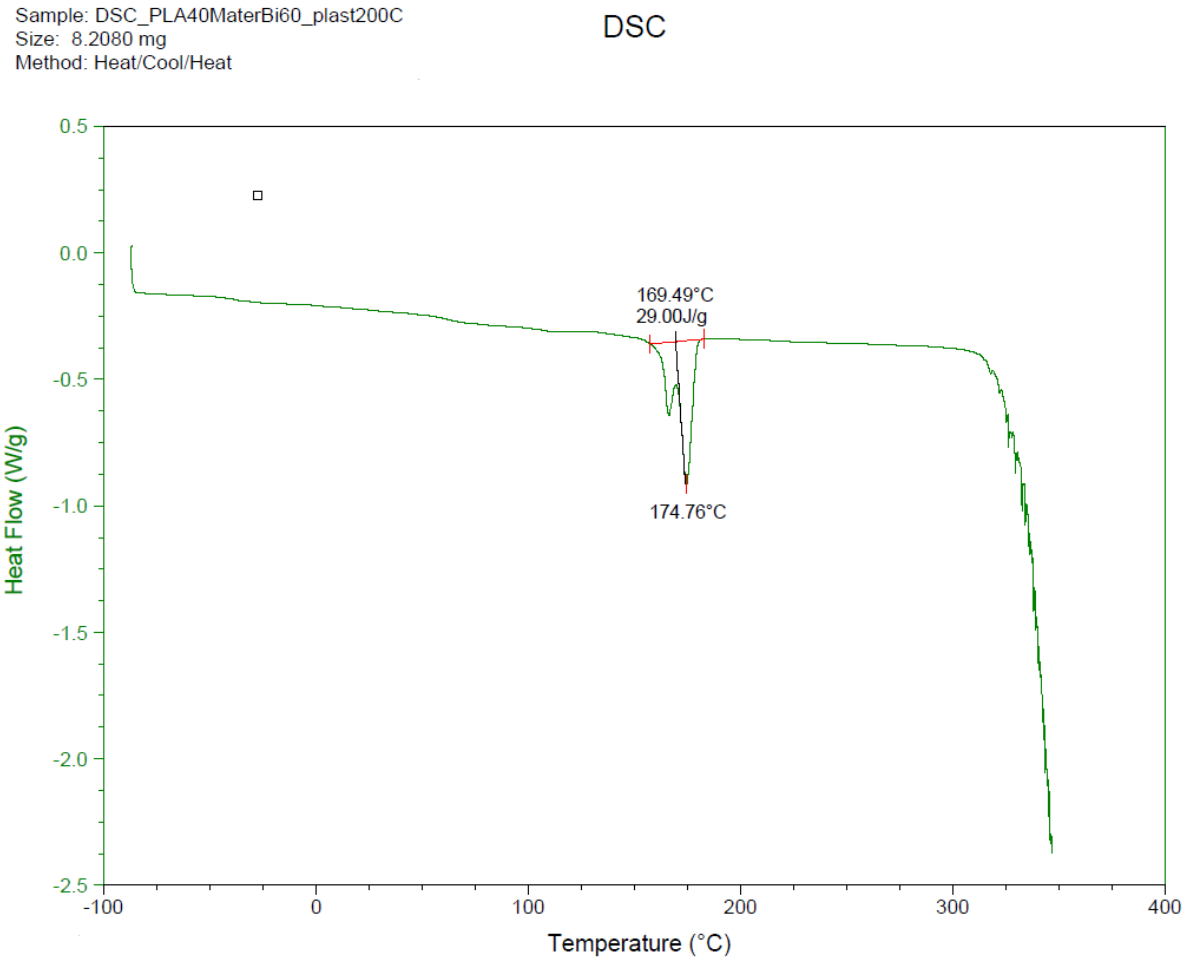


Graph 6.1- DSC curve of blend 7 (BioPBS/PCL)

On the other hand, blend between PLA and TPS seems to be compatible because, DSC shows only one peak in common with both materials. The table illustrates the Tm values, the figure the curve resulted. The unique peak is at 174.76 °C for blend of 40% PLA + 60% TPS. Several studies have been done on compatibility of PLA and TPS to reduce the disadvantages of both and the cost of finished products. Since both biopolymers exhibit opposite mechanical and barrier properties, their combination could lead to an improvement functionality. However, since TPS is highly hydrophilic and PLA is more hydrophobic, they are thermodynamically immiscible. The interfacial interaction between structures is poor, so researches[33] focus on improving their phase separation. Compatibilizers overcome this issue and can produce most effective materials[34].

Processing temperature of plastograph: 200°C	PLA/TPS	
	T_m TPS (°C)	T_m PLA (°C)
PLA100	-	Not appreciable
PLA80	176,44	Not appreciable
PLA60	175,88	Not appreciable
PLA40	174,76	Not appreciable
PLA20	172,81	Not appreciable
PLA0	169,26	-

Table 6.5- Tm for biopolymer blend 3 (PLA/TPS)



Graph 6.2- DSC curve of blend 3 (PLA/TPS)

Among all data, one interesting result is observable in blend of PLA with PHA. In ratio of 80% PLA + 20% PHA only one peak is visible. Although the analysis was replicated, the same result appeared. This is probably correlated to affinity of both materials in this specific relationship.

Processing temperature of plastograph 195°C	PLA/PHA	
	T_m PHA (°C)	T_m PLA (°C)
PLA100	-	175,94
PLA80	Not appreciable	174,94
PLA60	141,82	175,24
PLA40	142,55	174,95
PLA20	142,74	174,22
PLA0	142,74	-

Table 6.6- Tm for biopolymer blend 2 (PLA/PHA)

Compression moulding machine

More investigation on blends are done using compression moulding machine for preparing the specimens. It is important to underline that the decision to do DSC before starting the second step of analysis, is related to the fact that a re-melting occurs. In fact, re-heating materials may affect results and stability of biopolymers. The ISO 293: 2004 standard is referred only to thermoplastic materials, bioplastic's compression has not a regulation yet and therefore some experiments have to be performed on bioplastics. The temperatures used in compression moulding machine for biopolymers blends are the same performed with plastograph. On the other hand, for virgin bioplastic several tries were needed. The table 6.7 below shows the most suitable values and conditions meet in performing specimens after several tests.

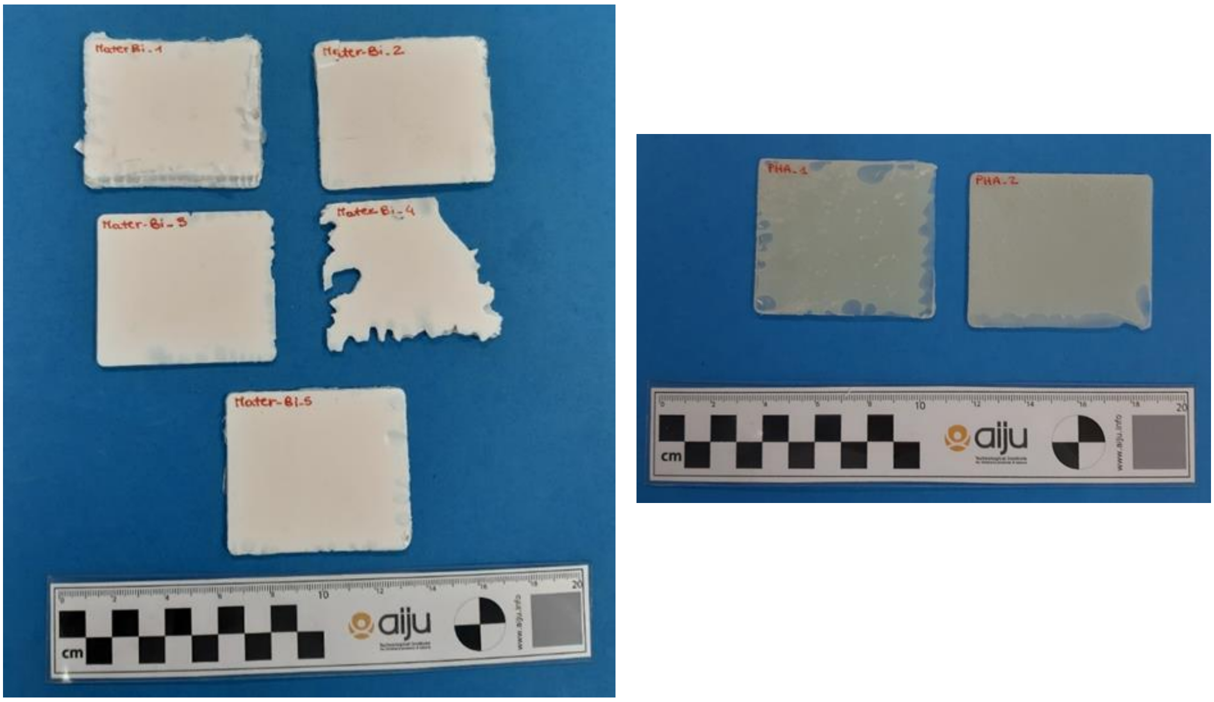
Blends	Temperature (°C)	Weight of sample (g)	Pression (MPa)	Pre-heating time (min)	Cooling time (min)
PLA 652 Ercros (PLA)	200	9	10	10 (air)	15
PH070 Ercros (PHA)	180	9	10	10	15
CAPA 6500 (PCL)	110	9	10	7 + 5 (*)	15
Mater-Bi EI51N0 (TPS)	210	9	10	10 (water)	15

(*) Melting TPS with the compressing machine shows some difficulties. After several attempts, it seems appropriate divide pre-heating time in two parts: first by leaving the materials on the aluminium sheets without press it, to promote melting (first value in the column). Later, once time has passed, inducing pressure to the mould (second value in the column).

PLA needs air for cooling because a brutal shock temperature breaks the specimen. This behaviour is due to PLA's rigidity. In cooling TPS faster, great results were shown by using water.

Table 6.7- Conditions used in compression moulding machine for virgin biopolymers

The data reported in the table 6.7 are the most suitable results met in testing virgin bioplastic. The photos 6.1 below show examples of tries performed with compression moulding machine at different conditions.



a) b)

Photo 6.1- Photo a) shows samples' tries with TPS. Photo b) shows samples' tries with PHA

Number of blends	Blends	Temperature (°C)	Weight of sample (g)	Pression (MPa)	Pre-heating time (min)	Cooling time (min)
1	PLA + PCL	200	9	10	10	15
2	PLA + PHA	195	9	10	10	15
3	PLA + TPS	200	9	10	6.5 + 5 (*)	15
4	PLA + PBS	200	9.5	10	10	15
5	PBS + TPS	190	9	10	6 + 7(*)	15
6	PBS + PHA	160	9	10	10	15
7	PBS + PCL	150	9	10	10	15
8	PHA + TPS	190	9	10	6.5 + 5(*)	15
9	TPS + PCL	190	9	10	10	15
10	PHA + PCL	160	9	10	10	15

(*) see table before

Table 6.8- Conditions in compression moulding machine for biopolymers' blends

Photo 6.2- Blend number 1 (PLA/PCL)

It is possible to notice that, at high quantities of PLA the rigidity of specimens increases, causing a possible break during the cooling time. This leads to unsuitable specimens for blend 1.

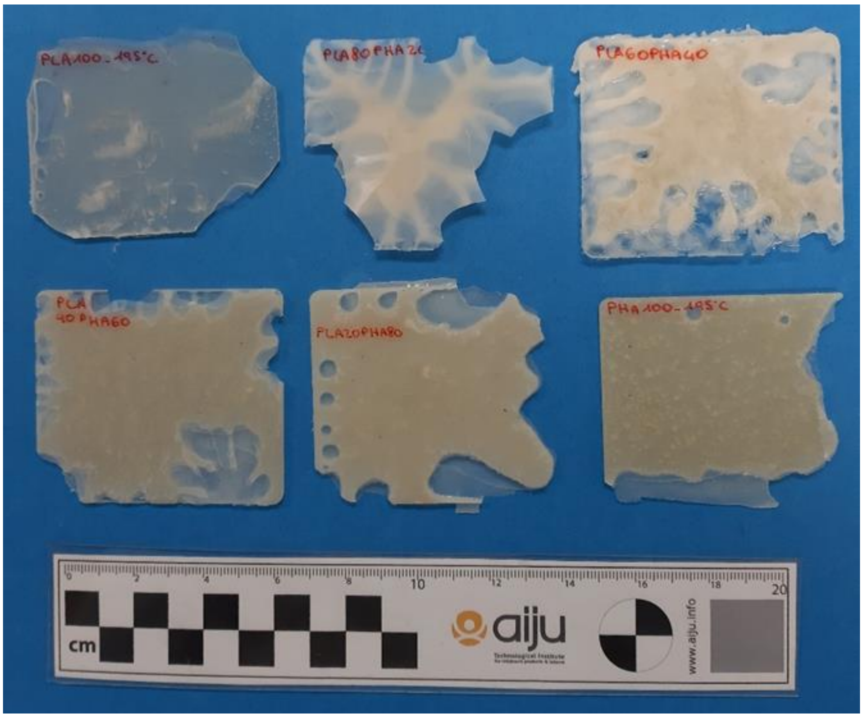


Photo 6.3- Blend number 2 (PLA/PHA)

It is visible that with high quantities of PLA the rigidity of blend 2's specimens can lead to a break. On the other hand, the presence of PHA gives malleability to specimens and enhances the flexibility.

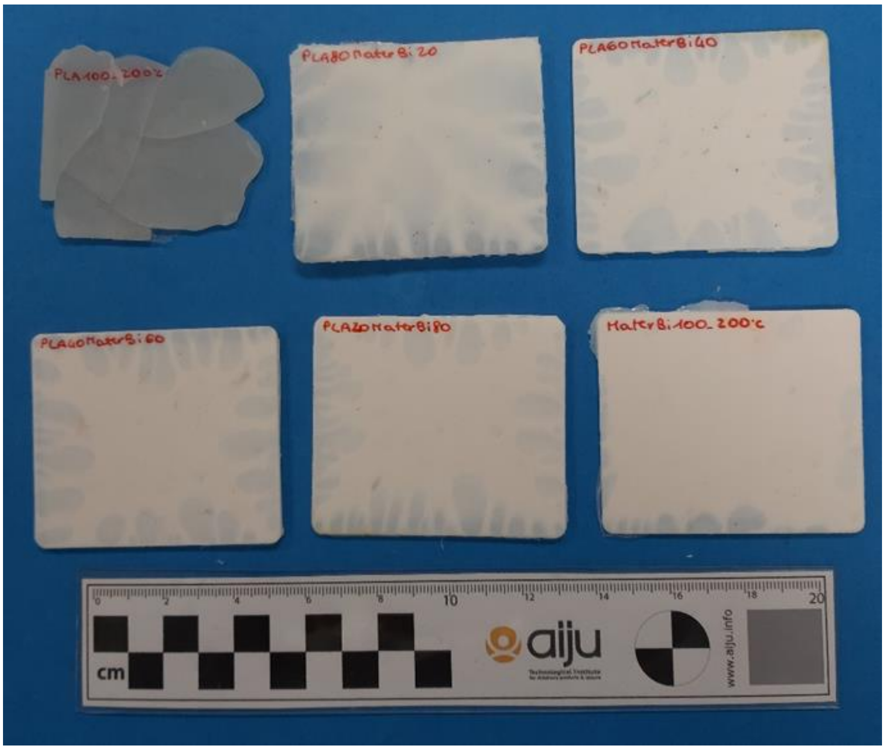


Photo 6.4- Blend number 3 (PLA/TPS)

The binary blend 3 performs quite homogenous specimens.

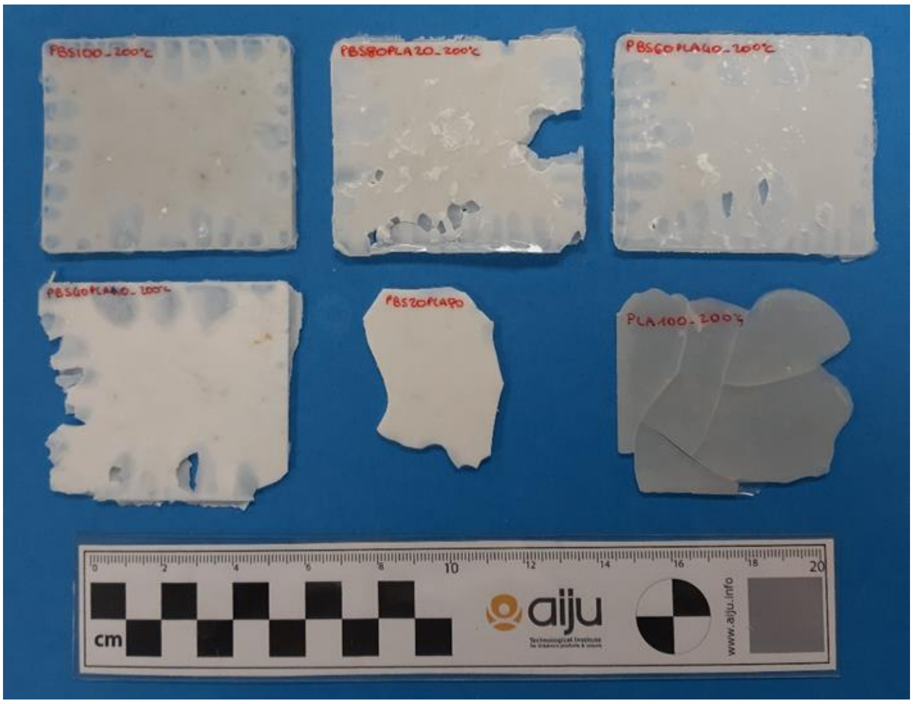


Photo 6.5- Blend number 4 (PLA/BioPBS)

The presence of BioPBS in blend 4 creates vacuum holes into specimens. These holes disappeared as the amount of PLA increased.

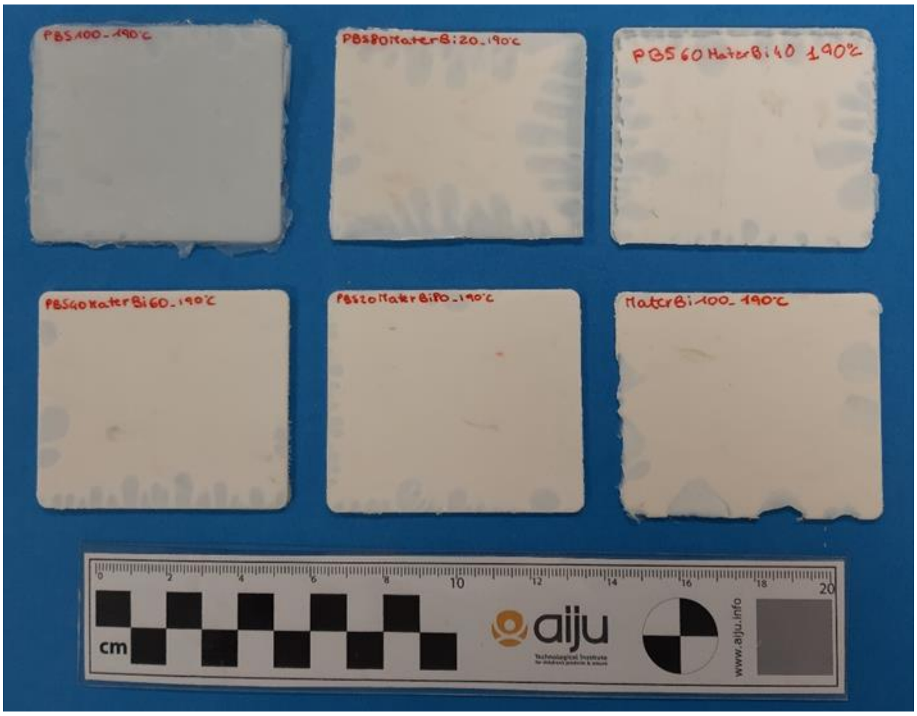


Photo 6.6- Blend number 5 (BioPBS/TPS)

The binary blend 5 performs quite homogenous specimens.

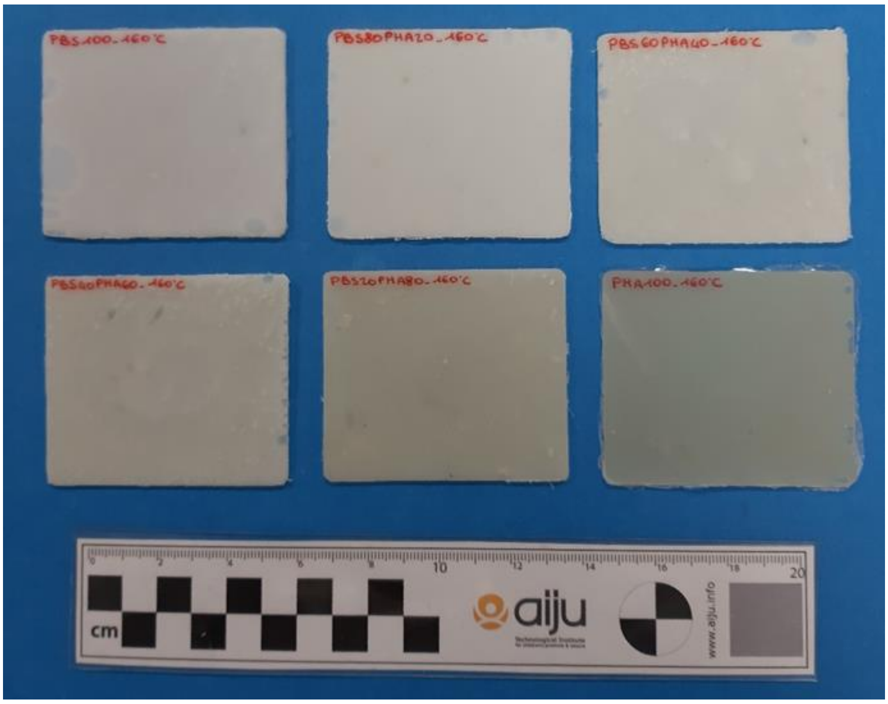


Photo 6.7- Blend number 6 (BioPBS/PHA)

The binary blend 6 performs quite homogenous specimens.

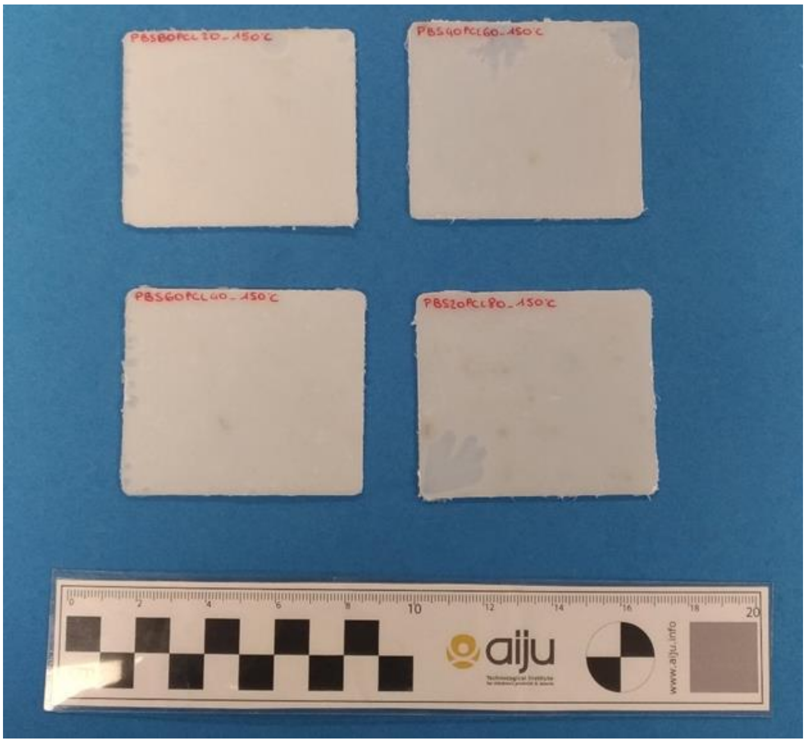


Photo 6.8- Blend number 7 (BioPBS/PCL)

The binary blend 7 performs quite homogenous specimens.

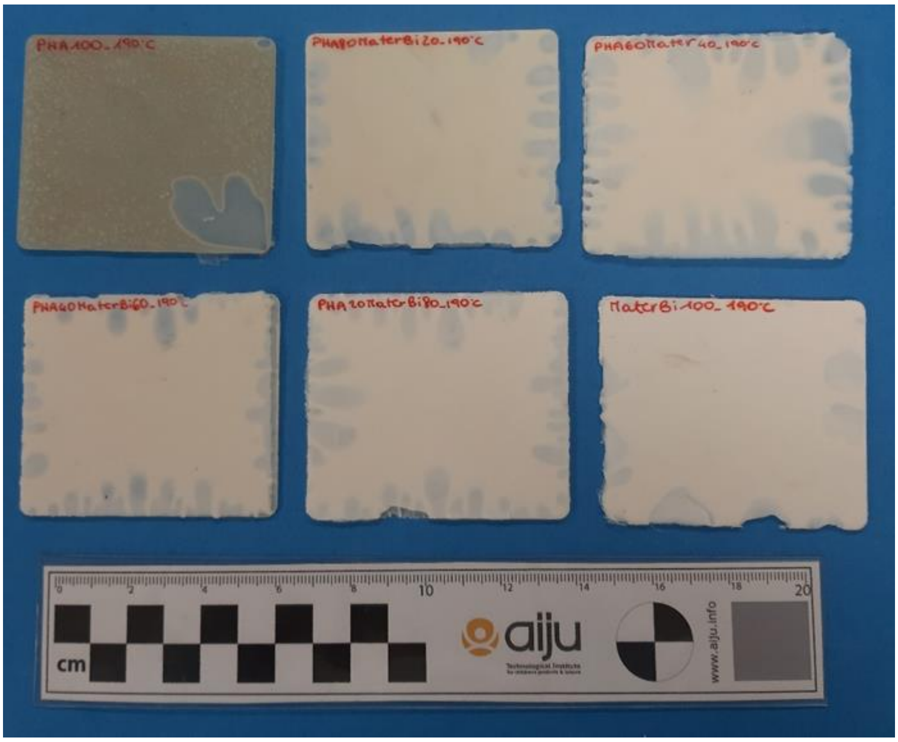


Photo 6.9- Blend number 8 (PHA/TPS)

The binary blend 8 performs quite homogenous specimens.

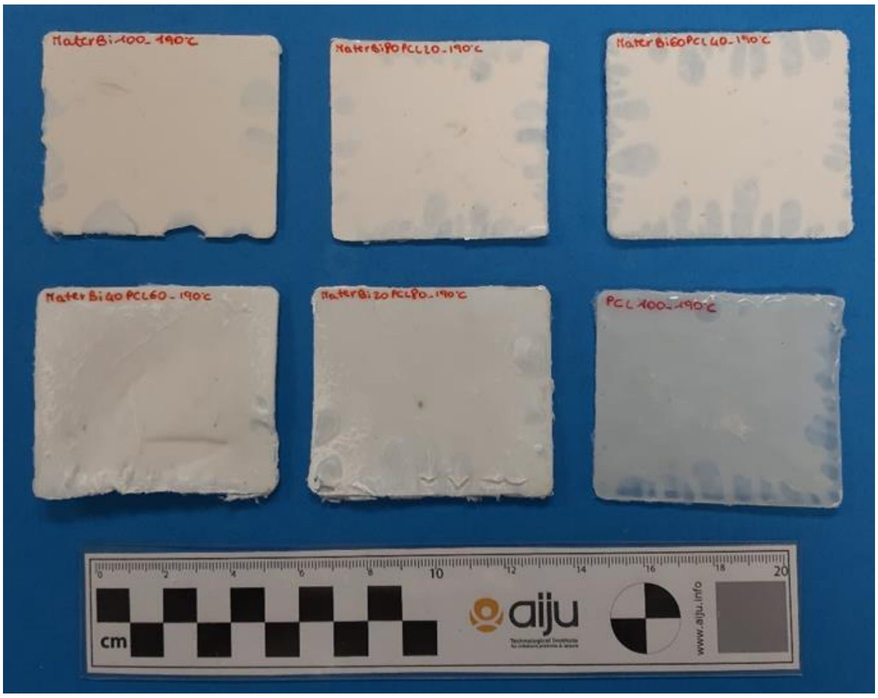


Photo 6.10- Blend number 9 (TPS/PCL)

The binary blend 9 performs quite homogenous specimens. However, it was difficult to separate the two aluminium sheets due to poor cooling rate of TPS.

Photo 6.11- Blend number 10 (PHA/PCL)

The binary blend 10 performs quite homogenous specimens.

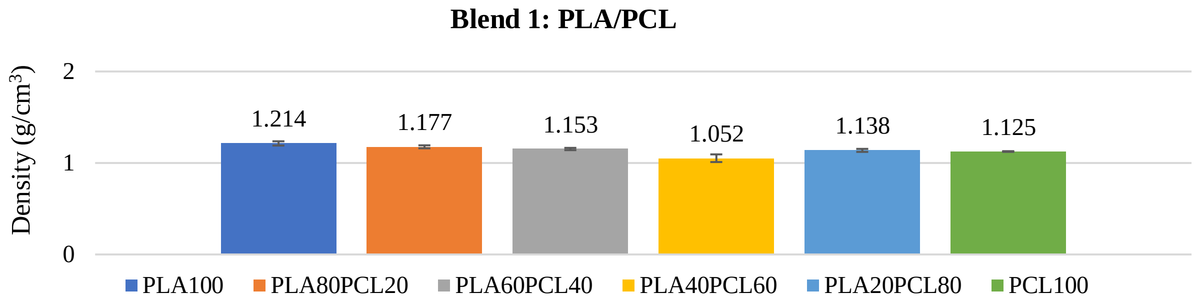
Once prepared the blend's specimens, further analysis have been done. Since the specimens do not comply legislations and regulations, they could be use just for density and hardness calculation. All the analysis were performed at room temperature, the average temperature in the laboratory was 22.2 °C.

Number of Blend	Analysis Measured	Biopolymer1 100%	80B1/ 20B2 (%)	60B1/ 40B2 (%)	40B1/ 60B2 (%)	20B1/ 80B2 (%)	Biopolymer2 100%
1	*Hardness (SHORE D)*	82,4	85,8	78,2	74,8	68,4	63,8
	Density (g/cm^3)	1,21	1,18	1,15	1,05	1,14	1,12
2	*Hardness (SHORE D)*	88,6	85,4	81	82	81,2	78,4
	Density (g/cm^3)	1,14	1,19	1,15	1,10	1,15	1,18
3	*Hardness (SHORE D)*	82,4	79,2	86	84	83	78,2
	Density (g/cm^3)	1,21	1,21	1,20	1,19	1,19	1,13
4	*Hardness (SHORE D)*	82,4	85,6	84,2	78,2	63,8	75
	Density (g/cm^3)	1,21	1,18	1,16	1,20	1,23	1,21
5	*Hardness (SHORE D)*	73,2	75,6	73	73	77	74,6
	Density (g/cm^3)	1,20	1,19	1,13	1,12	1,17	1,12
6	*Hardness (SHORE D)*	76,2	74,2	75	75,8	78,4	80,2
	Density (g/cm^3)	1,22	1,14	1,15	1,14	1,13	1,12
7	*Hardness (SHORE D)*	74,2	72,8	69,8	66,8	65,2	62,8
	Density (g/cm^3)	1,19	1,20	1,06	1,14	1,12	1,11
8	*Hardness (SHORE D)*	77,2	79,2	79,4	77	77,8	74,6
	Density (g/cm^3)	1,13	1,15	1,17	1,11	1,16	1,12
9	*Hardness (SHORE D)*	74,6	76,2	65,8	57,6	62	63
	Density (g/cm^3)	1,19	1,13	1,15	1,12	1,10	1,09
10	*Hardness (SHORE D)*	80,2	77,4	72,2	69	65	63,8
	Density (g/cm^3)	1,12	1,13	1,11	1,10	1,10	1,09

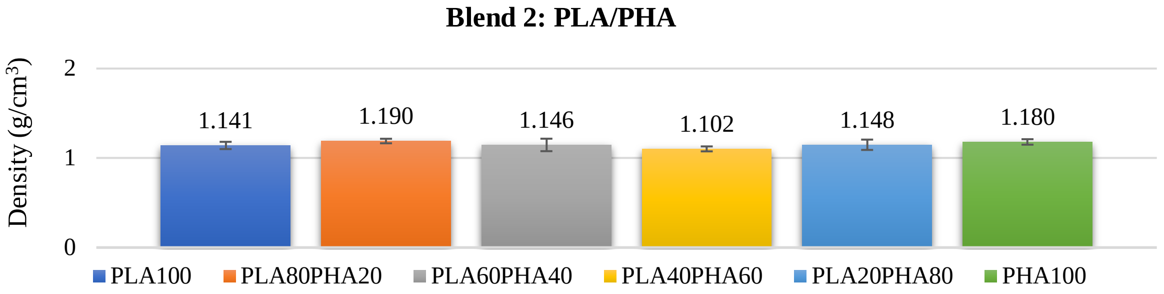
Table 6.9- Hardness and density values of all the biopolymers' blends

Density

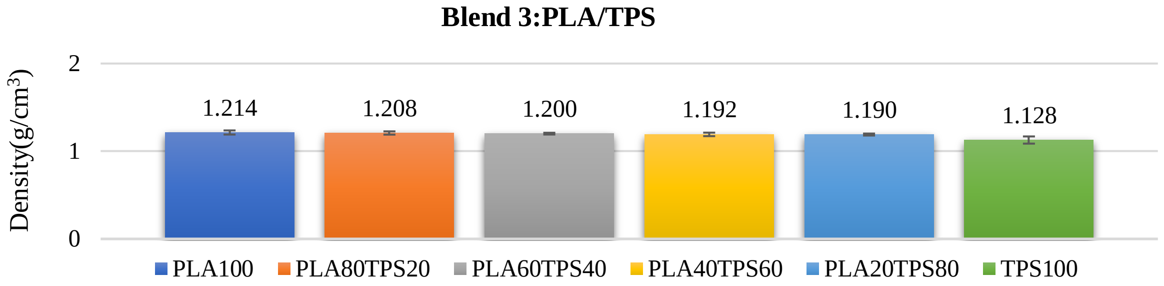
All the graphs below show the density values for each biopolymers' blends (from 1 to 10) in different percentages.



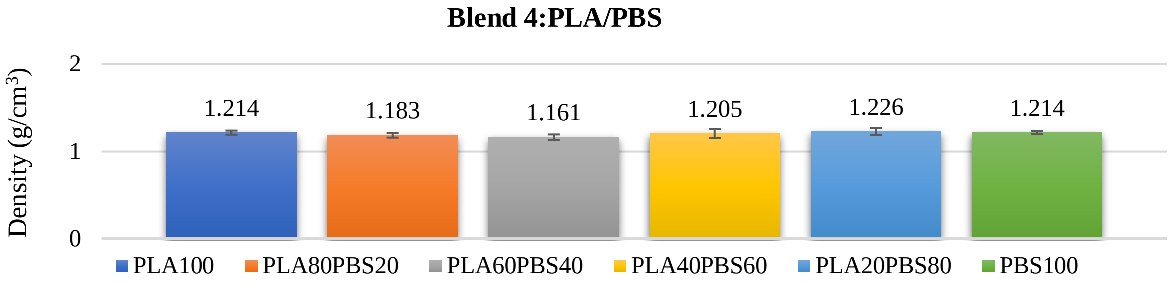
Graph 6.3- Density in blend number 1 (PLA/PCL)



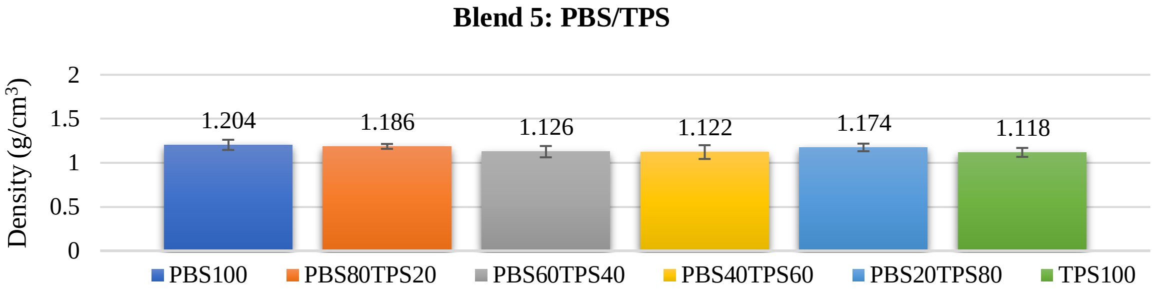
Graph 6.4- Density in blend number 2 (PLA/PHA)



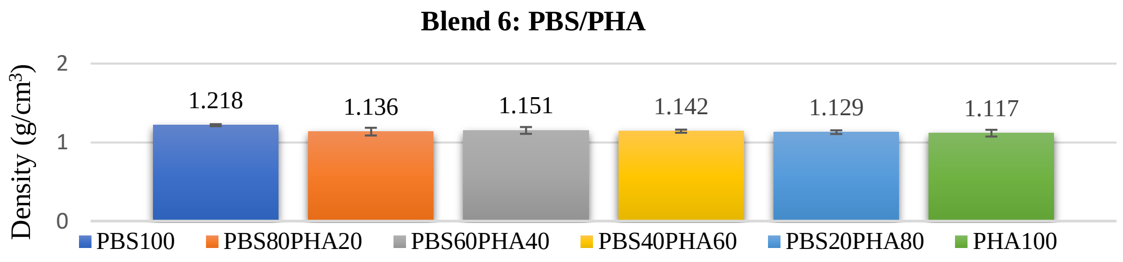
Graph 6.5- Density in blend number 3 (PLA/TPS)



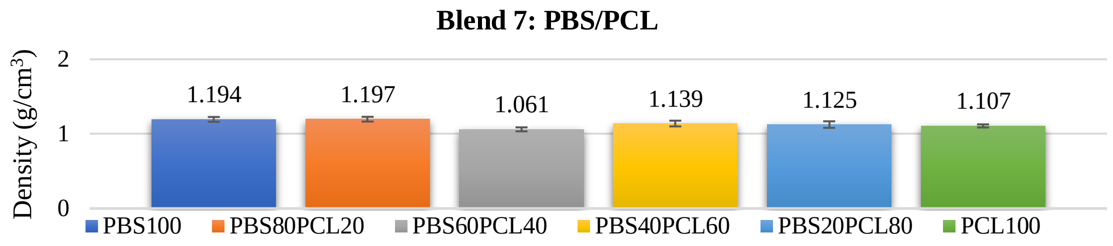
Graph 6.6- Density in blend number 4 (PLA/PBS)



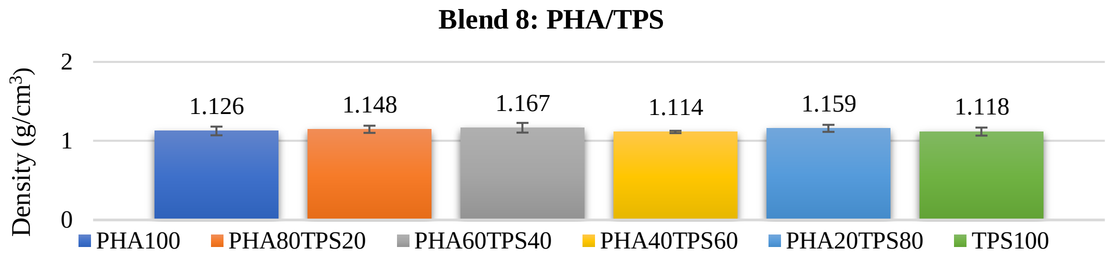
Graph 6.7- Density in blend number 5 (PBS/TPS)



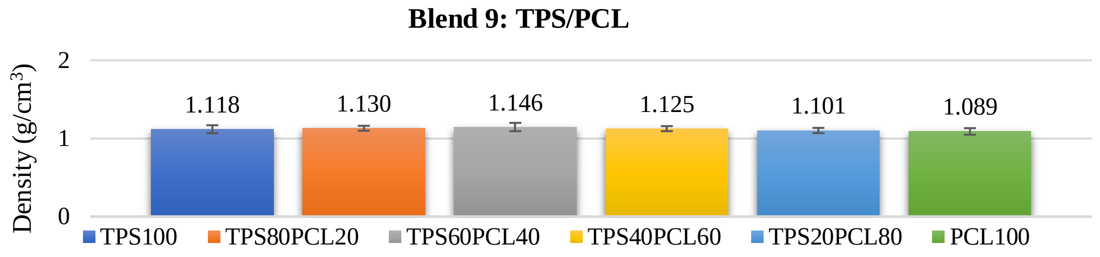
Graph 6.8- Density in blend number 6 (PBS/PHA)



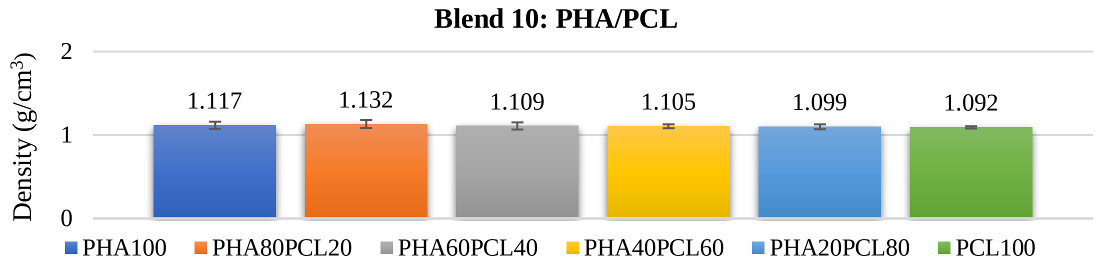
Graph 6.9- Density in blend 7 (PBS/PCL)



Graph 6.10- Density in blend 8 (PHA/TPS)

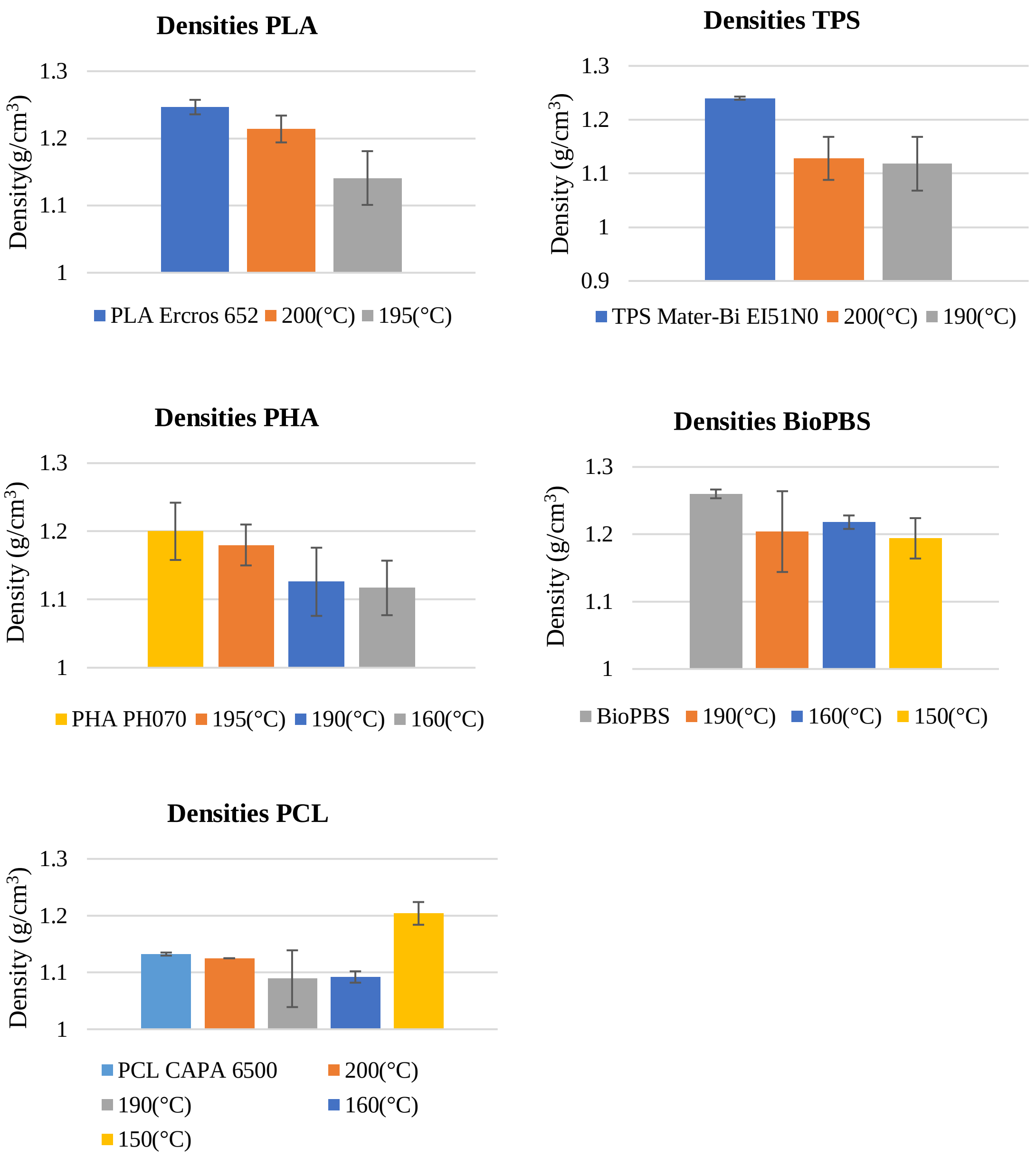


Graph 6.11- Density in blend 9 (TPS/PCL)



Graph 6.12- Density in blend 10 (PHA/PCL)

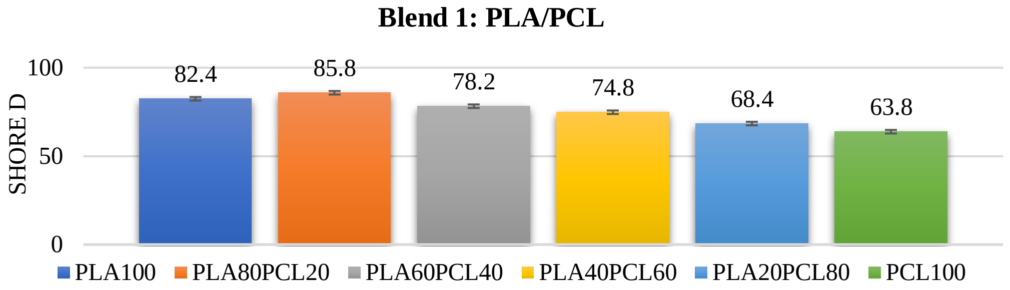
Through the visualization of data, it is possible to confirm that there are not any significant trends in blends' density. For this reason, it has been reasonable to investigate if temperature of processing could affect density. The graphs 6.13 below show different densities among virgin biopolymers by changing temperatures of processing samples. The first density value come from technical data sheets, while the others are originated from samples processing with compression moulding machine at different temperatures. Similarity between results of density could be linked to suitable temperature of processing samples. While a deviation from the technical data, may be related to unsuitable conditions of processing specimens with the machine.



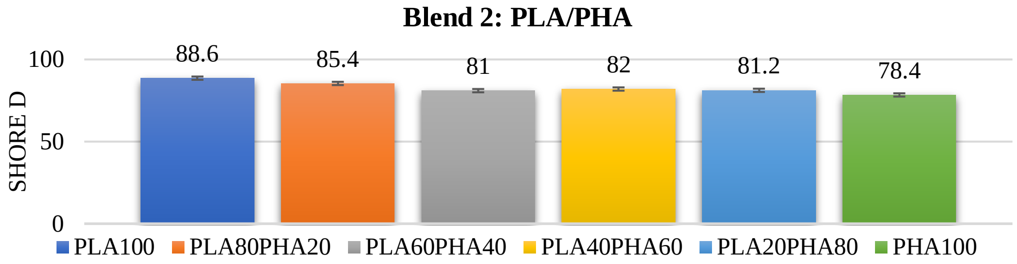
Graph 6.13- Variability in density of virgin biopolymers processed at different temperatures

Hardness

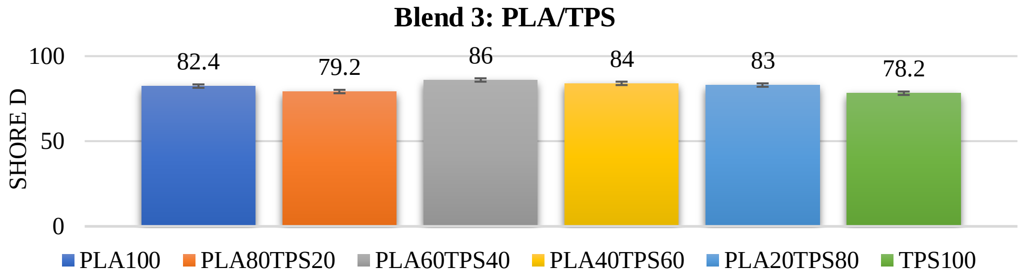
The graphs below show the hardness values of the blends. Hardness is a property that does not give many information about the behaviour of materials, since it presents very little variability in different blends, regardless of the changes in composition that are made. The hardness values remain stable even if the maximum peak is reached by PLA100 with its 88.6, while the lowest by 40% TPS and 60% PCL with 57.6. these values are results of the characteristics of materials. Respectively, PLA is much harder than all other materials. TPS/PCL materials show gummy behaviour that can be reflected in the value mentioned. However, it can be concluded that there are any significant trends and are within the margin of error of the deviation of these values. These considerations can be seen in the graphs represented as follow.



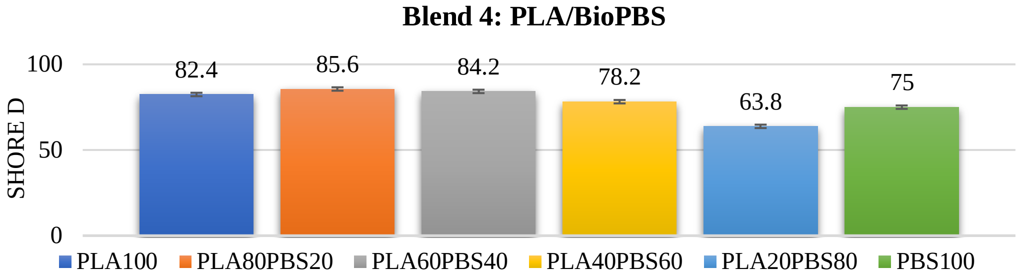
Graph 6.14- Hardness in blend 1 (PLA/PCL)



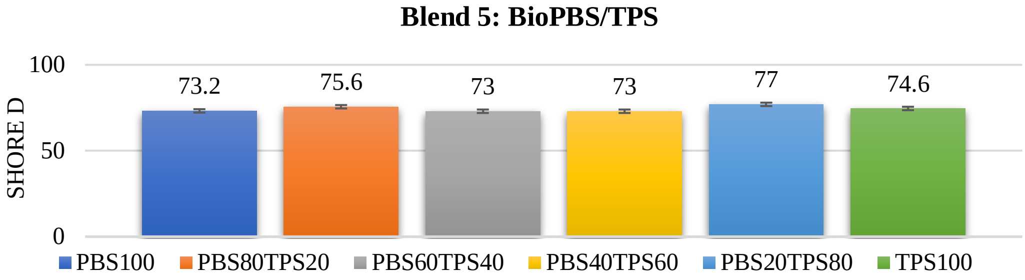
Graph 6.15- Hardness in blend 2 (PLA/PHA)



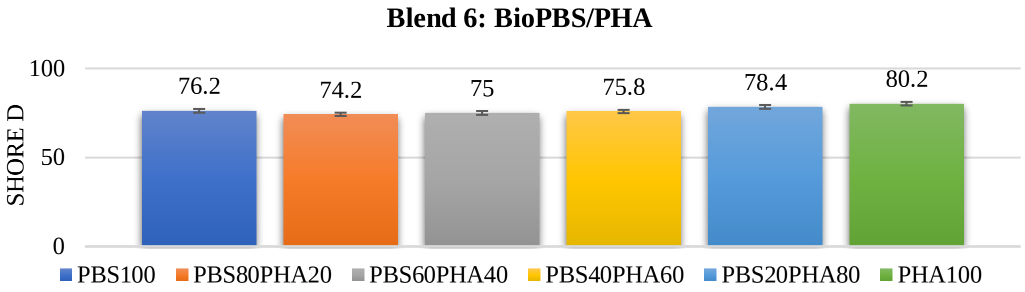
Graph 6.16- Hardness in blend 3 (PLA/TPS)



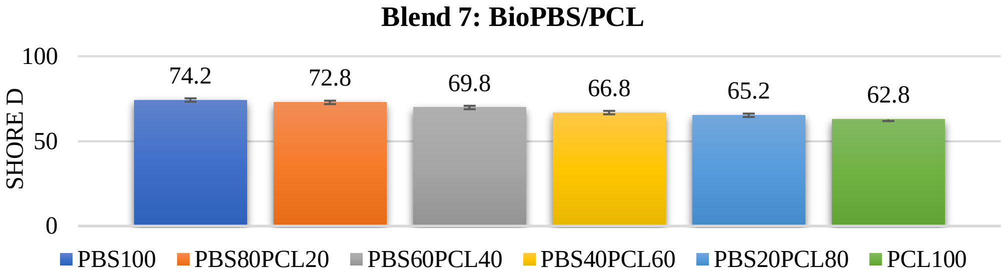
Graph 6.17- Hardness in blend 4 (PLA/BioPBS)



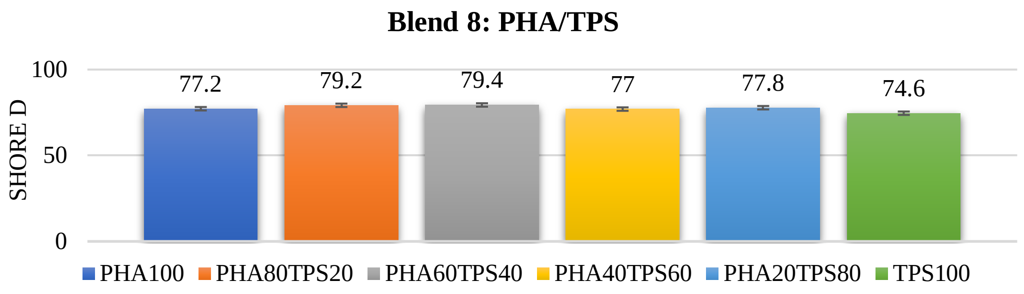
Graph 6.18- Hardness in blend 5 (BioPBS/TPS)



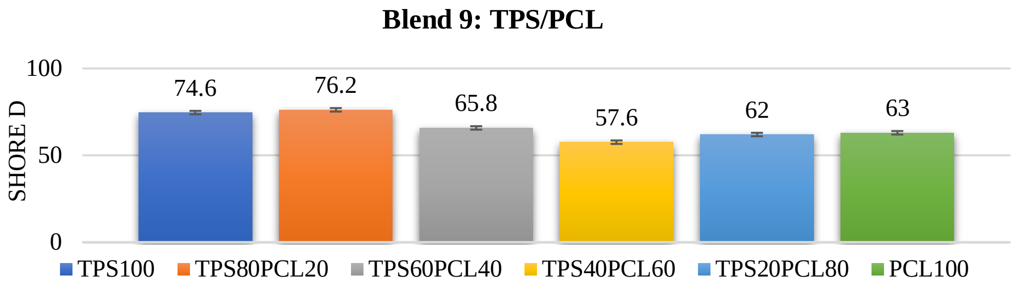
Graph 6.19- Hardness in blend 6 (BioPBS/PHA)



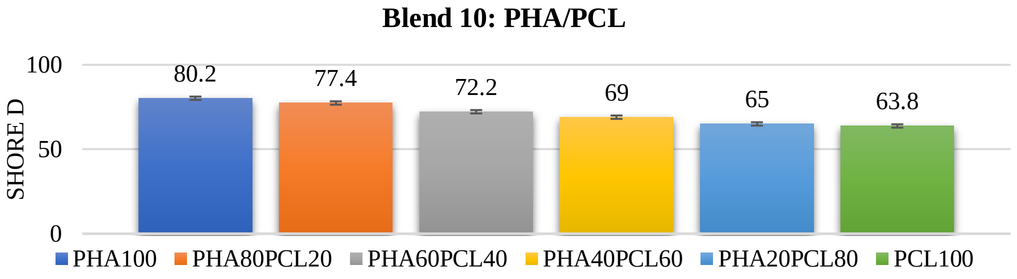
Graph 6.20- Hardness in blend 7(BioPBS/PCL)



Graph 6.21- Hardness in blend 8 (PHA/TPS)



Graph 6.22- Hardness in blend 9 (TPS/PCL)



Graph 6.23- Hardness in blend 10 (PHA/PCL)

6.2. Result 2

Improvement of mechanical properties of biopolymers' blends, with an increasing quantity of BioPBS in ratio 80-20% and 60-40%.

Among the biopolymers used in the work, BioPBS is a very promising material. BioPBS is generally blended with other compounds, to make its use more economical. Moreover, it shows excellent mechanical properties and can be applied in range of end applications via conventional melt processing techniques. BioPBS mechanical and thermal properties are very close to those of widely used conventional plastic, particularly polyethylene (PE) and polypropylene (PP). The aim of investigation is decreasing the rigidity of biomaterials blends and improving their mechanical properties by using BioPBS. At room temperature BioPBS behaves as a ductile polymer, it has low toughness and stiffness values. Additionally, BioPBS has a glass transition temperature (Tg) of about -35°C and melting point (Tm) of around 114°C, whose let it suitable in processing.

Preparation of specimens

The blends of biopolymers include PLA/BioPBS, TPS/BioPBS and PHA/BioPBS. Blends were performed in ratio 80-20% and 60-40% respectively, in a total of 3 kg each.

Percentage in blends	Weight in blends
80 - 20 (wt.%)	2.4 – 0.6 kg
60 - 40 (wt.%)	1.8 – 1.2 kg

Table 6.10- Respectively weights in blends 80-20% and 60-40%

Before injecting blends into the moulding machine, it is necessary dry biopolymers to eliminate the moisture catch during the storage. Since the moisture content for BioPBS is less than 0.01%, it has been decided to use it as such. While for the other materials drying was necessary. For each material 3.6 kg were drying according to properties revealed in the technical data sheet. The table 6.11 shows the parameters selected for drying.

Material	Time (hour)	Temperature (°C)
PLA	5	80
TPS	3	50
PHA	5	80

Table 6.11- Parameters used for drying biomaterials with Dry-Air mini.

The biomaterials will use for preparing 1A type of specimens with injection process. The standard specimens are necessary for the analysis which follow. In using injection machine many parameters must be manipulated. The tables below illustrate the variations of conditions during the injection to perform more suitable specimens.

PLA + BioPBS	80-20 (%)	60-40 (%)
Temperature (°C)	210-210-200-190-50	210-210-200-190-50
Temperature mould (°C)	35	35
Velocity (cm^3/s)	60	60
Time compaction (s)	15	15
Pression compaction (bar)	400	500
Cooling time (s)	60	60
Loading speed (rpm)	100	100

Table 6.12- Conditions in injection machine during the specimens' preparation for blend of PLA and BioPBS.

Photo 6.12- Represent example of specimens injected. To the left 80-20% and to the right 60-40% of blend PLA/BioPBS

TPS + BioPBS	80-20 (%)	60-40 (%)
Temperature (°C)	220-220-200-180-50	220-220-200-180-50
Temperature mould (°C)	30	30
Velocity (cm^3/s)	60	60
Time compaction (s)	20	20
Pression compaction (bar)	420	500
Cooling time (s)	40	40
Loading speed (rpm)	100	100

Table 6.13- Conditions in injection machine during the specimens' preparation for blend of TPS and BioPBS.

Photo 6.13- Represent example of specimens injected. To the left 80-20% and to the right 60-40% of blend TPS/BioPBS

PHA+ BioPBS	80-20 (%)	60-40 (%)
Temperature (°C)	160-160-150-140-50	160-160-150-140-50
Temperature mould (°C)	35	35
Velocity (cm^3/s)	30	30
Time compaction (s)	30	30
Pression compaction (bar)	350	350
Cooling time (s)	80	80
Loading speed (rpm)	100	100

Table 6.14- Conditions in injection machine during the specimens' preparation for blend of PHA and BioPBS.

Photo 6.14- Represent example of specimens injected. To the left 80-20% and to the right 60-40% of blend PHA/BioPBS

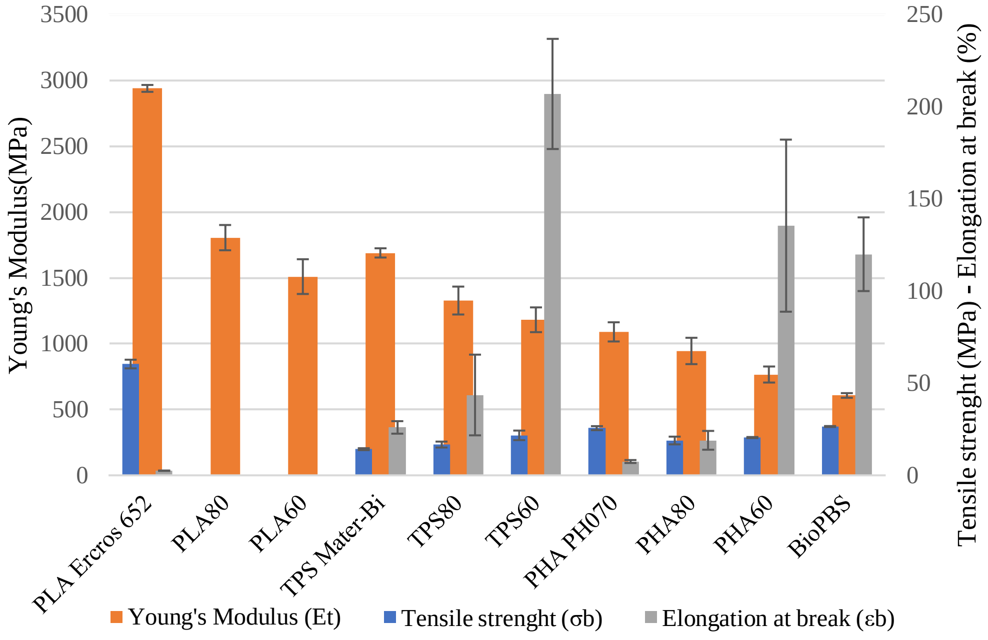
For blend 1 (PLA/BioPBS) there were some problems during the injection. Particularly difficult was finding right condition in cooling time for specimens. The rigidity of PLA creates issues in extracting samples from the mould. It has been decided to change and increase temperature in the machine's profile. In this way, the extraction was facilitated, however the specimens had darker colour rather than the initial material (avory). This consequence may be due to degradation and burnt of blends. For this reason, they were not subjected to tests.

Mechanical characterization

Traction, Flexion and Charpy tests were analysed. The average value is the result of ten repetitions of test in each specimen. A set of mechanical behaviour of blends are summarized in table 6.15.

Table 6.15- Summary of the mechanical properties of the biopolymers' blends obtained by mechanical tests (tensile stress (σb); tensile modulus or Young (Et); elongation at break (εb), density calculation, test Charpy impact and hardness (SHORE D).

Material	**σb (MPa)**	**Et (MPa)**	**εb (%)**	**Density (g/cm^3)**	**Charpy Impact (kJ/m^2)**	**Hardness (SHORE D)**
PLA80	-	1806±96	-	1.24±0.08	18.75±1.54	81±1.7
PLA60	-	1510±132	-	1.22±0.02	31.6±7.99	82±2.6
TPS80	16.7±1.6	1328±106	43.6±21.9	1.23±0.01	4.6±0.8	76±0.4
TPS60	21.7±2.6	1182±94	207±29.9	1.24±0.01	4.62±1.03	75±0.4
PHA80	18.9±2.1	945±100	19±5.1	1.21±0.01	1.91±0.16	76±0.8
PHA60	20.5±0.3	766±61	135.5±46.7	1.22±0.01	2.33±0.1	76±1.3
PLA Ercros 652	60.4±2.35	2940±26.1	2.5±0.11	1.25±0.01	17.42±1.94	85±1
PHA PH70	25.6±1.09	1090±72.9	7.5±0.79	1.26±0.003	63.48±17.98	51±1
TPS Mater-Bi	14.2±0.52	1690±35.1	26±3.4	1.14±0.04	6.23±0.75	73±1
BioPBS	26.5±0.26	607±17.7	120±20	0.92±0.007	4.90±1.17	73±1



Graph 6.24- Graph with values of Young's modulus (Et), Tensile strenght (σb) and Elongation at break (Ɛb) for virgin biopolymers and blends 80-20 and 60-40 with BioPBS.

Young's Modulus relates stress to strain in the basic principle that a material undergoes elastic deformation when it is compressed, returning to its original shape when the load is removed. More deformations occur in flexible materials. As can be seen in graph 6.22, the maximum value of Young’s Modulus is represented by PLA. The value reflects PLA’s stiffness or resistance to elastic deformation under load. Comparing blends’ values is notable that Young’s Modulus follows a decreasing trend as the BioPBS quantity increases. This result is what is expected on adding a ductile, flexible polymer to a more rigid one. Generally, lower values reflect more elastic blends, while rigid polymers have high moduli. PLA tends to be strong to break, but not to be very tough caused by its brittle.

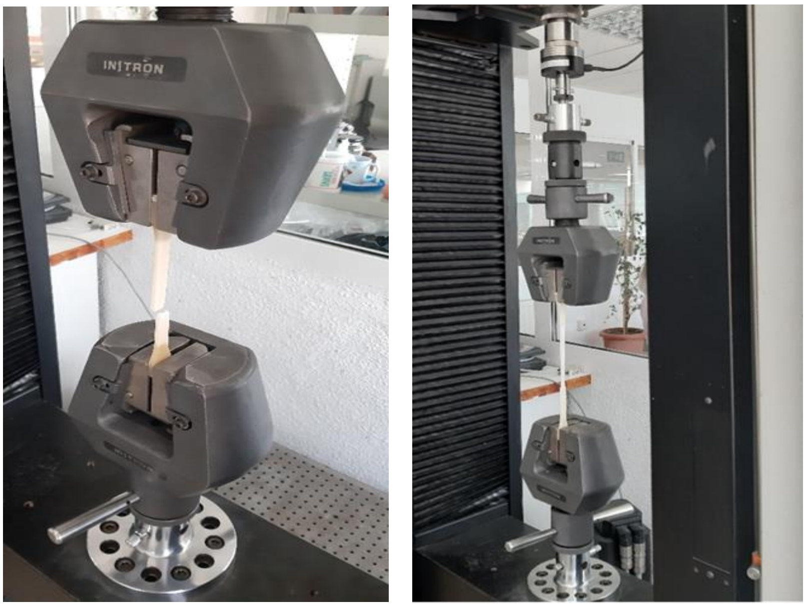
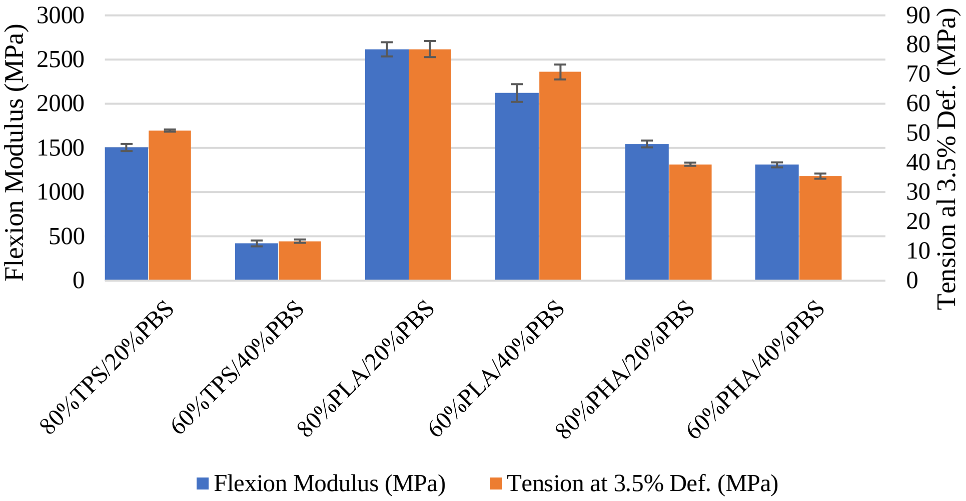


Photo 6.15- Photos of specimens during the Traction test

Tensile strength is the maximum amount of stress that it can be subjected to a material before failure. Stress means strength and it is calculated in MPa. However, all strengths concern to how much stress is needed to break specimen. Elongation at break, is the ratio between increased length and initial length after breakage of the tested specimen. The elongation is expressed in percentage (%) and basically refers to ductility of specimens. It can be notice from the table (6.15) that values for Tensile strength and Elongation at break do not concerning PLA blends. This is due to the inability of these blends to resist under tensile stress and elongation in the machine. The high stiffness of PLA does not allow to complete the standardized tests. Further improvement and studies in mixtures may be investigated.

Other necessary test in dictate polymer’s mechanical properties is flexural test. Flexibility provides ability to resist deformation under load. The values are significantly different from the tensile modulus because the stress pattern in the specimen is a combination of tension and compression. Data are useful for comparing the strength and stiffness, Flexural modulus denotes the capacity to bend and it gives a measure of stiffness of materials. The value is proportional, higher the flexural modulus, the stiffer the material. On the contrary, the lower the flexural modulus, the more flexible it is. Same trend is shown by deformation (%). For ISO 178 the test is stopped when the specimen breaks. If the specimen does not break, the test is continued as far as possible and the stress at 3.5% is reported (conventional deflection), as it is stated in the graph 6.24. The most drastic decreasing slope in Flexural Modulus can be seen for TPS and PLA. PHA has already good flexibility and the addition of BioPBS does not affect too much the ductility in blends.



Graph 6.25- Flexural Modulus and tension to 3.5% deformation for blends 80-40 and 60-40 with BioPBS

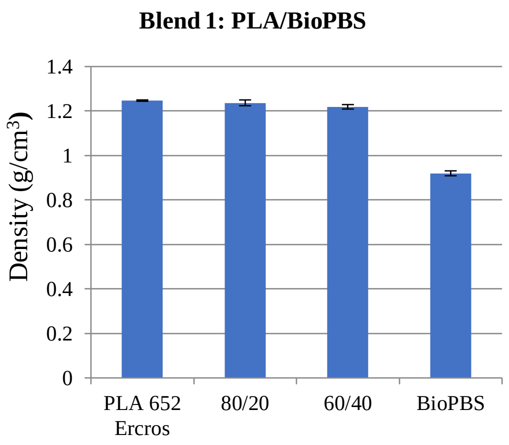
Comparing the data of virgin biopolymers with those of biopolymer-blends, it is notable that the addition of BioPBS weakens the rigidity and increases resistance to deformation, by improving the modulus of flexibility. It is known that a flexible polymer has high elongation at break, because of high ductility. The use of BioPBS is a valuable strategy to decrease blends rigidity and increase their renewable content. As proof of concept, TPS and PHA blend showed very good flexibility and high value of elongation at break. On the other hand, the addition of BioPBS to PLA provoked a strong decrease in values till the impossibility to end the standardized performances.

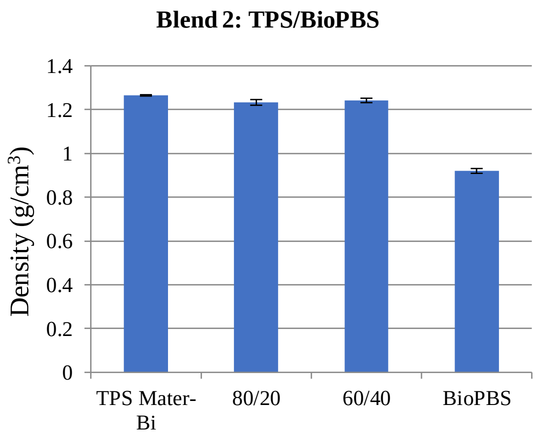
The Charpy impact test is a complementary analysis that summarizes the conclusion to tensile strength and deformation at break. Charpy determines the amount of energy a material can absorb when impacted by a large impulse. Impact strength is an important indirect design parameter to consider in terms of plastic structures because it quantifies how a material withstand sudden shocks. In fact, specimens can be notched or unnotched according to materials' resistance to impacts. Generally, it is used to determine toughness of a material. With toughness is intended the ability to resist both fracture and deformation when force is applied. According to values, it can be summarized that a rubberier character gives higher elongation at break and better impact resistance values, although such materials have lower stiffness.

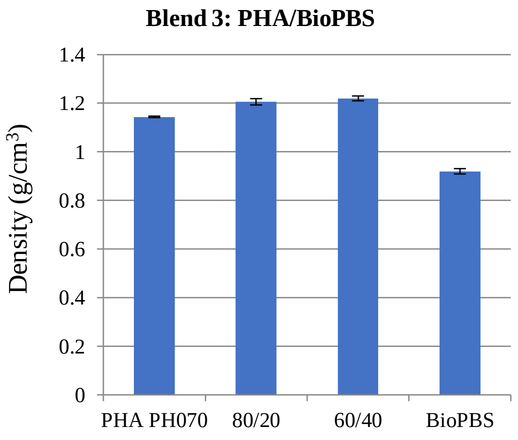
In case of blends tests, all impacts cause total breaks of specimens. Only for PLA a pendulum of 5 Joule was used. This is due to greater degree of crystallinity of polymer that cause it harder behaviour, resulting in facility to break samples without notch specimens. On the other hand, the specimens made for blends with TPS and PHA needed notch, in order to facilitate the analysis. In these cases, a pendulum of 1 Joule was sufficient. Even if values come from the same standard test, it is not possible to compare results because performing with different pendulums (1 and 5 Joule). However, it is important to stand out that a raise in concentration of BioPBS leads to increasing Impact strength.

Density

Graphs 6.25 visualize the values of density (g/cm^3) calculated at room temperature (around 22.2°C). The blends of biopolymer have an intermediate density between those of virgin materials. It can be concluded that the performance is notable.







Graph 6.26- Graphs represent density in blends 80-20% and 60-40% BioPBS

Hardness

Hardness data are collected at room temperature using SHORE D. It is notable that there is not a remarkable trend. For this reason, it has been decided to not represent values on graphs. Generally, the addition of BioPBS should decrease rigidity and consequently hardness of blends. On the contrary, for blends of PHA/BioPBS hardness gains 3 points.

6.3. Result 3

Development and improvement of mechanical properties and complementary thermal analysis of PLA with percentages of VINNEX® ranging from 5 to 20% through injected samples.

Wacker experts declare that VINNEX® enables the combination of different biopolymer raw materials giving advantages in critical characteristics of bioplastics. VINNEX® is especially compatible with PLA enhancing its property profile. Specifically, blending VINNEX® powder with PLA demonstrated improvements in impact strength, enhancing flexibility and compatibility with other biopolymers. VINNEX® is basically an ethylene vinyl acetate (VAc-E), an extremely elastic and tough thermoplastic. Vac-E has many attractive properties including low cost, good flex-crack and impact resistance and it is used with other plastics in blends. In blends the percentage of Vac-E ranges from 2 to 25%. Generally, the addition of this copolymer reduces the melting point and improves the low temperature performance. VINNEX® 2504 is recognized to offer great miscibility with PLA and great processability together. The percentages investigated ranging from 5 to 20% ratio. The high cost of VINNEX® powder let prepare the starting blend with the highest percentage (20%) of additive, for then diluting it in lower ratios for the other mixtures.

Preparation of specimens

Since materials for blends are in two shapes (powder and pellet), the extrusion was necessary before the injection. The extrusion machine helps to amalgamate the powder (additive) to pellets (PLA) forming a continuous profile. For creating a homogenous blend, materials were subjected to double extrusion. In a total of 6 kg each, the ratio was 80% wt. of PLA and 20% wt. VINNEX® 2504 powder. Performed at same conditions, the filament created at the end of each extrusion was pelletized and dehumidified. Specifically, after the first extrusion blend was dried in oven at 80°C for 90 minutes. While after the second one, Dry-Air Mini performed drying process at 70°C for 4 hours.

Material	80% PLA + 20% VINNEX® 2504							
Total passage of material	10 kg/h							
Pressure of melted material	4 bar							
Temperature of melted material	202 °C							
Screw velocity	70 rpm							
Temperature of zone (°C)	TZ8	TZ6	TZ5	TZ4	TZ3	TZ2	TZ1	TZ7
	195	195	195	190	190	190	40	0

Table 6.16- Conditions in the extrusion machine for preparing sample 80% PLA – 20% VINNEX

Once the second extrusion is concluded and pelletized material dried, blend is ready for injection moulding. From this blend, the other mixtures were prepared, respectively with 5-10-15% of additive. The operation was a dilution of the starting blend (20% wt. of VINNEX®).

Blend PLA + VINNEX®	5%	10 %	15%	20%
Temperature (°C)	200-200-190-180-50	200-200-190-180-50	200-200-190-180-50	200-200-190-180-50
Temperature mould (°C)	35	35	35	35
Velocity (cm^3/s)	60	60	60	60
Time compaction (s)	10	10	10	10
Pression compaction (bar)	550	550	550	550
Cooling time (s)	40	60	40	40
Loading speed (rpm)	100	100	100	100

Table 6.17- Conditions in the injection moulding machine for preparing specimens of blend PLA+VINNEX at 5-10-15-20%

Photo 6.16- Photo of specimens prepared. Starting from the left: PLA+5% VINNEX; PLA+10% VINNEX; PLA+ 15% VINNEX; PLA+ 20% VINNEX

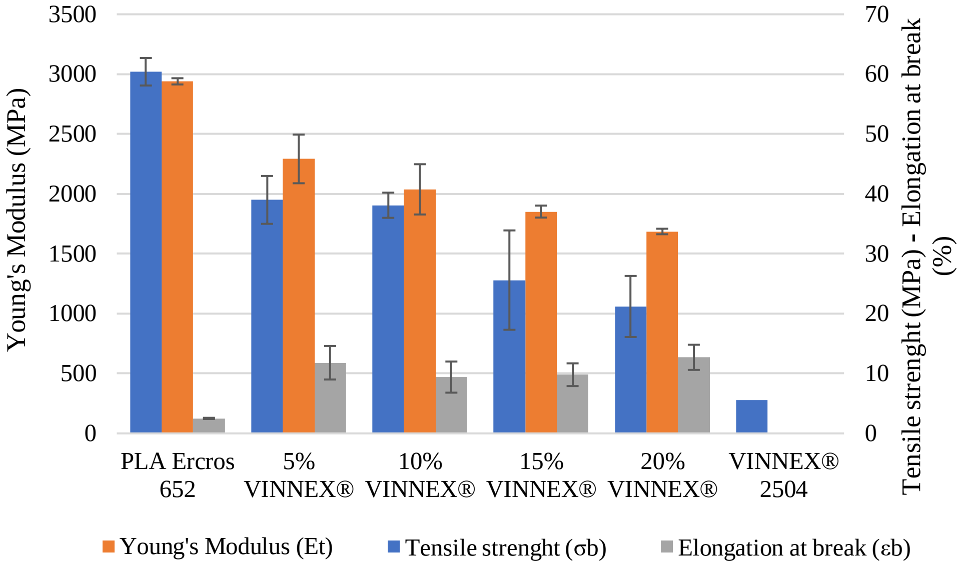
Mechanical Characterization

Traction, Flexion and Charpy tests were analysed. The tests were performed on each specimen and duplicated. A set of mechanical behaviour of blends are summarized in table 6.18 below.

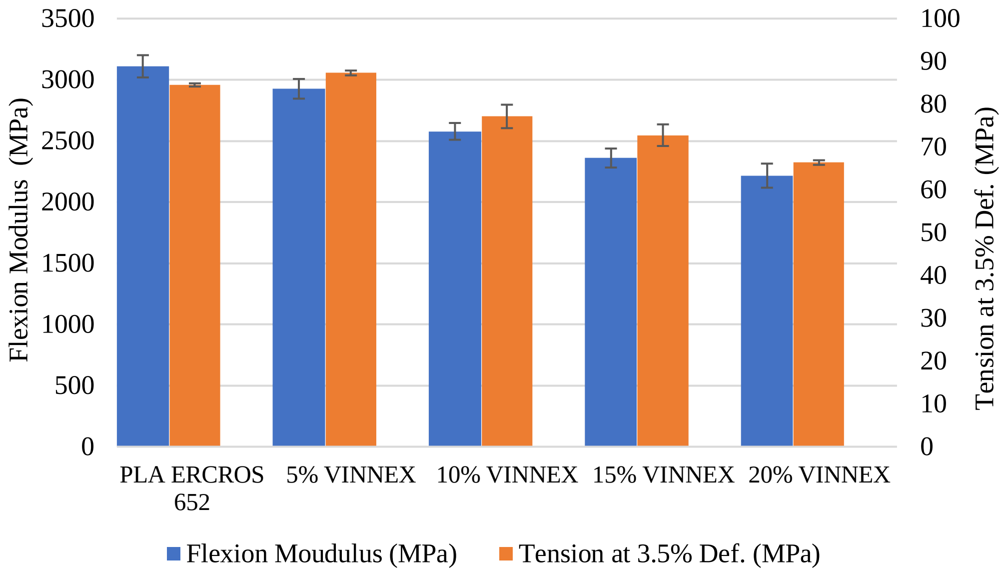
Table 6.18- Summary of the mechanical properties of the biopolymers' blends obtained by mechanical tests: tensile strength (σb); Young modulus (Et); elongation at break (εb), density calculation, test Charpy impact and hardness.

Blend PLA	σb (MPa)	Et (MPa)	εb (%)	Density (g/cm^3)	Charpy Impact (kJ/m^2)	Harness (SHORE D)
5% VINNEX®	39±4	2292±203	11.8±2.8	1.22±0.02	49.33±7.91	87±1
10% VINNEX®	38.1±2.1	2038±210	9.4±2.6	1.21±0.03	60.12±4.33	84±1
15% VINNEX®	25.6±8.3	1852±50	9.8±1.9	1.20±0.03	78.15±17.07	85±1
20% VINNEX®	21.2±5.1	1686±23	12.7±2.1	1.19±0.03	3.93±0.78	86±1
PLA 652 Ercros	60.4±2.35	2940±26.1	2.5±0.1	1.25±0.01	17.42±1.94	85±1
VINNEX® 2504	5.56	0.11	498	1.23	-	-

Tensile behaviour is measured with test specimens. It is notable that the values tent to decrease with raising of additive's concentrations. Same trend is shown by Young's Modulus. By increasing additive's quantity, the blends become more flexible as demonstrates the lowers Young's moduli. The values are expected as result of addiction of VINNEX®, which is extremely elastic material. Chemically, VINNEX® is amorphous polymer; this means that the random molecular jumble lets the chains move across each other when the polymer is pushed or pulled. This is why, VINNEX® donates flexibility and rubbery behaviour to blends.



Graph 6.27- Graph with values of Young's modulus (Et), Tensile strenght (σb) and Elongation at break (Ɛb) for PLA Ercros 652 and blends with additive VINNEX at 5-10-15-20%

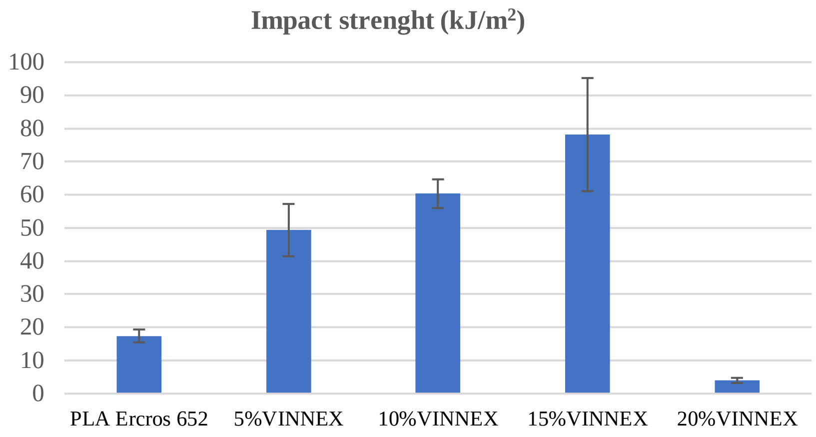


Graph 6.28- Flexion Modulus of PLA Ercros 652 and blends with additive VINNEX at 5-10-15-20%

Flexural modulus is illustrated in detail for each percentage in the graph 6.26. According with stated before, the increasing amount of additive raises the flexibility of blends, although the values numbers decrease.

Blends PLA	Impact strenght (kJ/m²)	Dev.standard	Type of break	Joule	Notch
PLA 652 Ercros	17,42	1,94	Total	1	No
5% VINNEX	49,33	7,91	Total	5	No
10% VINNEX	60,33	4,33	Total	5	No
15%VINNEX	78,15	17,07	Total	5	No
20 % VINNEX	3,98	0,78	Total	1	Yes

Table 6.19- Impact strength with Charpy test for PLA with additive VINNEX in 5-10-15-20%



Graph 6.29- Impact strength with Charpy test for PLA with additive VINNEX in 5-10-15-20%

The graph 6.27 shows an increasing in impact strength as the additive raises. A part for the blend PLA+20% VINNEX®, the others were performed at same conditions and impact with 5 Joule pendulum without be notched. On the other hand, as the flexibility increases with the additive content, 1 Joule pendulum for blend of 20% was not able to break the specimen. Therefore, to facilitate the measure, samples were notched.

As concerning hardness, not particularly interesting trend is presented. Values are stable around 85 ± 1 SHORE D. While, for density it is notable that tends to decrease as the content of VINNEX® increases. This can be due to addition of additive. When mixing materials, the free volume in polymer structure increases. Generally, an additive gets in between the polymer chains and spaces them apart from each other, causing larger volume that results in a decrease of density.

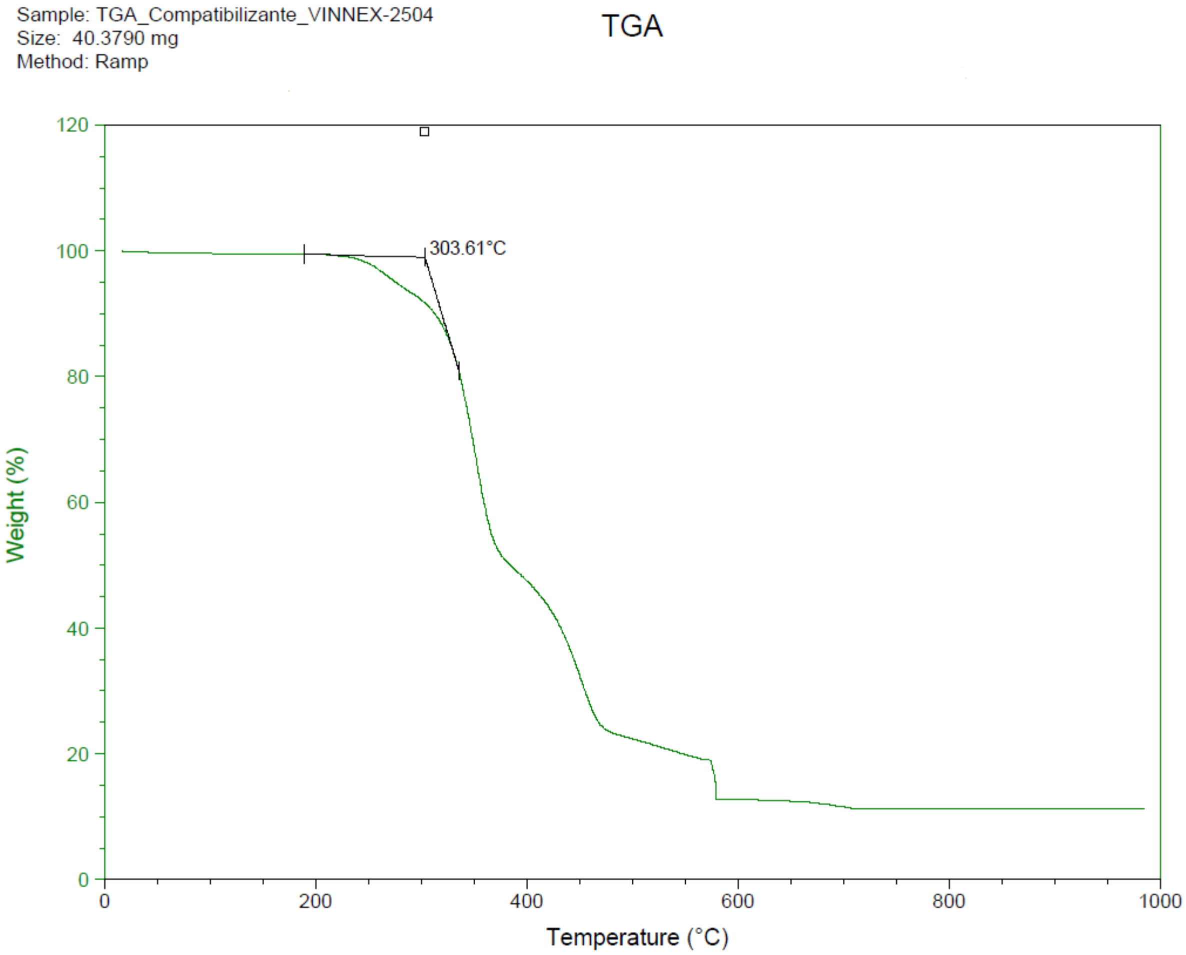
From technical data sheet, it is already tested that VINNEX® is an impact modifier for PLA, by improving its behaviour. The excellent combination of properties that VINNEX® offers, makes it useful for various markets. Blend's improvements in mechanical, processing features make VINNEX® ideal for many applications compared to pure PLA.

Thermal Characterization

Thermal analysis was done by DSC and TGA. The DSC gives information about melting temperature. PLA has a melting temperature of 174.68°C, while the VINNEX® blends in different percentages stay closed to this value (approximately 175°C). On the other hand, for pure VINNEX® 2504 is not possible to evidence melting temperature as it does not have one. In fact, VINNEX® 2504 is an amorphous polymer and presents only a glass transition temperature, where the polymer translates from rigid to softer state.

By DSC analysis, it was found a discordant value for glass temperature (Tg) from technical sheet of VINNEX® 2504. Wacker company declares a Tg at -7°C, while the analysis done in the laboratory gave a Tg of 0.40°C. The mismatching can be related to mistakes during analysis as the analysis has not been replicated. The low value of Tg permits to additive having great mobility chain because molecules start wiggling above this temperature. Lower Tg value is exploited by different uses of compounds.

TGA evidences the temperature at which starts degradation. In particular, the graph 6.3 below illustrates the degradation temperature of VINNEX® 2504 around 303°C.



Graph 6.30- Curve of TGA where the degradation of VINNEX starts

Concluding, it is important to point out the benefits in adding the additive to PLA. Improvement in mechanical features can be underlined. Especially, the new blends offer a family of materials that can be processed as the conventional ones through injection moulding, extrusion, thermoforming without modified thermoplastic equipment. VINNEX®, with greater combination of flexibility and tough even at low temperature, is able to replace more dangerous compounds. Moreover, Wacker guaranties its totally sustainability. Company declares that blending biopolymers with additive improve stiffness without affecting biodegradability, making them suitable for disposable. Wacker opens the path for a new generation of products which benefit the environment and improve processability. However, investigation on biodegradability of VINNEX® blends' have not been tested.

6.4. Result 4

Comparison between biopolymers' blends with and without addition of 10% VINNEX® 2504.

After studying the benefits of blending VINNEX® with PLA only, it makes sense investigate on further blends. PLA is one of the most studied material, on which additional researches look into for the future. In the exploration, the ratio 60% of PLA and 40% of other biopolymers seems the most promising. The proportion was chosen because it is a great compromise for maintaining PLA qualities at cheap costs. The same logic is followed by the percentage of VINNEX®. It seems meaningful find an intermediate ratio which contributes to adding (or not) benefits to biopolymers' blends. The work was developed by comparing previously blends of PLA in proportion 60-40% with other biopolymers, with the addiction or not of 10% VINNEX®. The thermal characterization follows DSC and TGA analysis. The specimens were prepared by compression moulding machine and used for measuring density and hardness.

Preparation of specimens

As the previous operations, blending PLA with other biopolymers was done by using plastograph. Apart VINNEX® powder, the other biopolymers are under pellet shape. Before the melting operation in plastograph, the materials were rightly weighted. Considering the capacity of the equipment (40 g), the proportions were calculated on the total.

Respectively, each blend contains 10 PHR of VINNEX®. PHR (part per hundred resin) is the amount of additive to be added per hundred parts of the materials in the compounding mixture. The table shows the different PHR in blends in a total mixture mass of 40 grams.

Materials	PHR
PLA	60
Second biopolymer	40
VINNEX® 2504	10

Table 6.20- Blends of biopolymers in different percentage where the additive VINNEX where added at 10%

The processing temperature in the plastograph are listed in the table 6.21. There are not any differences between the blends previously prepared. In this way the results can be compared, without the possibility having interferences.

Number of blend	10% VINNEX	Temperature in plastograph (°C)
1	60PLA + 40 PCL	200
2	60PLA + 40PHA	195
3	60PLA + 40TPS	200
4	60PLA + 40PBS	200

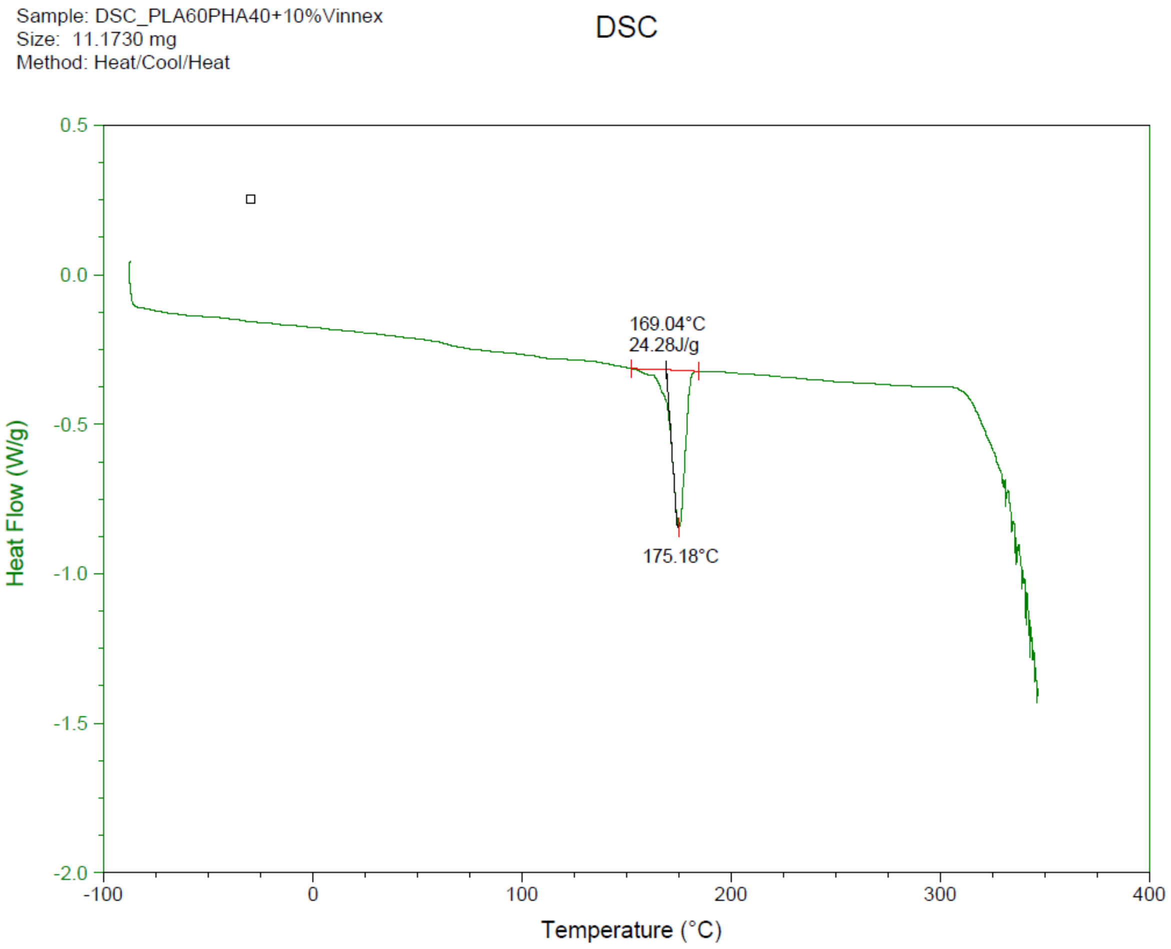
Table 6.21- Conditions used in the plastograph for blends with 60%PLA and 40%of different biopolymers and VINNEX at 10%

Thermal characterization

After being pelletizing, all the blends are characterized by thermal analysis (DSC an TGA) and compared with the biopolymer blends that do not contain VINNEX®. It was seen the same results as the previous blends, confirming the incompatibility between biopolymers. Considering the melting temperatures in the second heating cycle, blends 1 and 4 did not show compatibility among the materials in the mixtures. The components in these blends present distinct melting temperatures as synonymous of incompatibility. The Tm accords with those of virgin bioplastic materials. However, as regarding PLA/PHA + VINNEX® (blend 2), it is appreciable only one peak that coincides with PLA's melting temperature (around 175°C). This can suggest that both materials with additive can be compatible in the percentages chosen.

Processing temperature in plastograph 195°C	PLA/PHA	
	T_m PHA (°C)	T_m PLA (°C)
PLA60 PHA40	141,82	175,24
PLA60PHA40+10%Vinnex		175,18

Table 6.22- Tm from DSC analysis for blend 60%PLA-40%PHA and 10% VINNEX

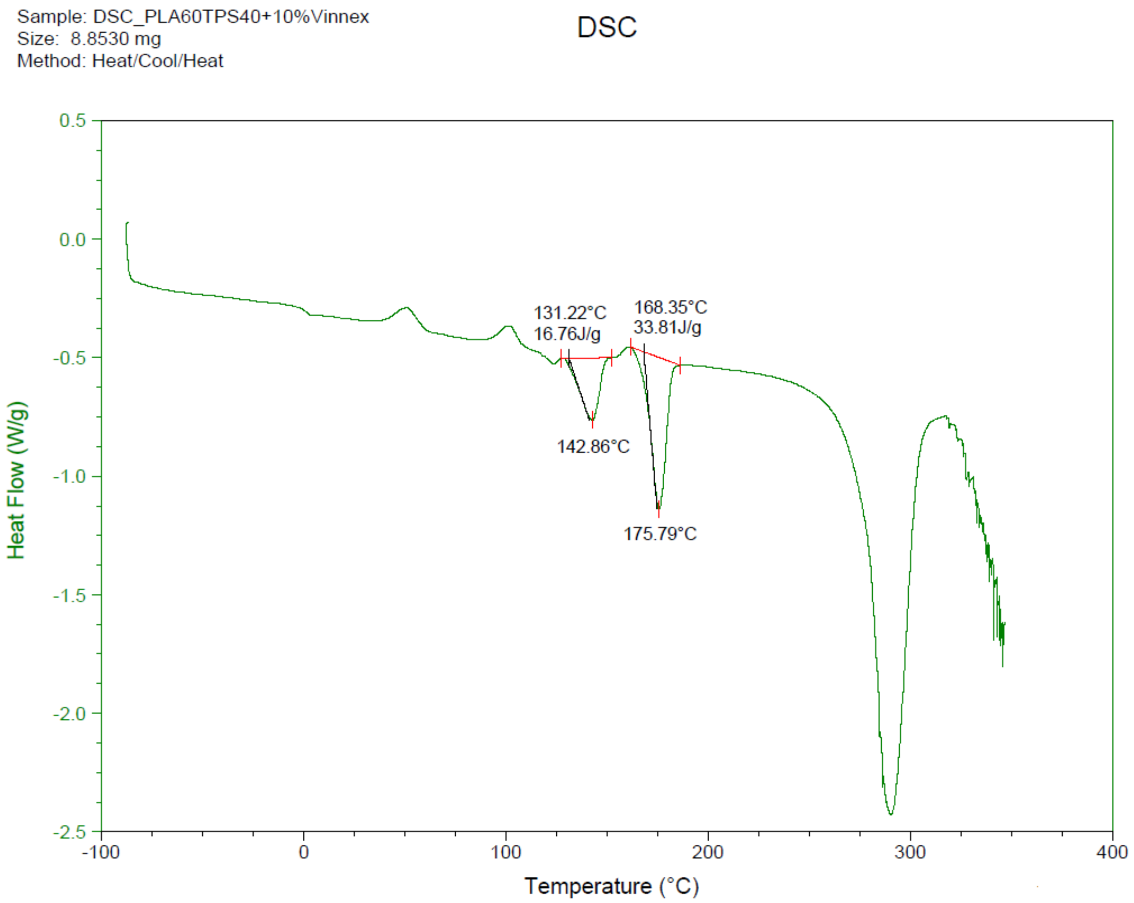


Graph 6.31-DSC curve of 60%PLA/40%PHA and 10% VINNEX

the only possible compatibility was appreciated in blend of PLA/TPS. If before they show only one peak at 174.76°C, now the situation is reversed. It seems that the apparent compatibility disappears in presence of VINNEX® 2504. From the graph is possible notice that there are two different peaks. However, while one coincides with Tm of PLA 652 Ercros, the other does not match with TPS Mater-Bi EI51N0 (169.45°C). There is a regression shift in the curve.

Processing temperature in plastograph 200°C	**PLA/TPS**	
	T_m TPS (°C)	**T_m PLA (°C)**
PLA60 TPS40	175,88	Not appreciable
PLA60TPS+10%Vinnex	142,86	175,79

Table 6.23- Tm from DSC analysis for blend 60%PLA-40%TPS and 10%VINNEX



Graph 6.32- DSC curve for blend 60% PLA-40% TPS and 10% VINNEX

Mechanical characterization

For the investigation on hardness and density of blends, the specimens were prepared with compression moulding machine. The conditions of temperature and time do not vary from the previous used for processing the biopolymer blends. For each analysis, the result is average of five repetitions for hardness and ten for density. The values are reported in table below according to each blend.

Number of Blend	**Analysis Measured**	**60PLA**	**60PLA+ VINNEX®**
1	*Hardness (SHORE D)*	78.2±1	72.4±1
	Density (g/cm^3)	1.15±0.01	1.14±0.02
2	*Hardness (SHORE D)*	81±1	75.6±1
	Density (g/cm^3)	1.15±0.07	1.15±0.04
3	*Hardness (SHORE D)*	86±1	79.2±1
	Density (g/cm^3)	1.20±0.01	1,15±0.05
4	*Hardness (SHORE D)*	84.2±1	79±1
	Density (g/cm^3)	1.16±0.05	1.18±0.02

Table 6.24- Comparison of Hardness and density of blends 60%PLA and 40% of other biopolymers with and without 10% VINNEX

If for density values there is not a linear trend, hardness shows a visible decreasing by adding the additive in the blends. As mentioned before, the addition of VINNEX® improve flexibility to the detriment of hardness. The change in the hardness can be found in matrix thanks to interaction between the three materials. However, as the mixing was done with plastograph the uniform distribution may be not perfectly efficient. VINNEX®'s addition provides more flexibility and less hard blend turn into. In any case, as proved before, the supplement of VINNEX® increases every mechanical property in blends.

7. CONCLUSION

Conclusion according to specific results.

1. *Compatibility of biopolymers in various percentages analysed through DSC, TGA. Further investigations on hardness and density in specimens prepared with compression moulding machine.*

Thermo-analysis studied the compatibility of bioplastics. DSC identifies if a binary blend shows compatibility between compounds by the presence of one peak in melting temperature. During the investigation, the results in biopolymers' blends give potentially for investigating on compatibility between PLA and TPS. DSC's second heating cycle shows a curve with one peak in common. This melting temperature is the combination of both Tm's materials. However, further investigations need to be developed.
The standard specimens for the mechanical analysis are prepared through compression moulding machine. Since there is not a regulation which defines the more suitable conditions for processing bioplastic specimens, several tries were necessary. The final specimens were results of manipulation of parameters as temperature, pression and heating/cooling time. It has been seen that density's results may be affected by temperature of processing. Deviations from technical data can be related to unsuitable conditions of samples' performing.

2. *Improvement of mechanical properties of biopolymers' blends, with increasing quantity of BioPBS in ratio 80-20% and 60-40%.*

BioPBS has a gummy and ductile behaviour. It has been decided to prepare bioplastics binary blends with BioPBS in order to visualize how behave. Bio-blends were tested mechanically to verify how the increasing content of BioPBS reflect on elasticity in mixtures. Blends decline their rigidity at the expenses of flexibility. Standard specimens show great resistance to deformation and impact tests, letting blends to expand their possible applications. Furthermore, the processing operation used conventional equipment making their manufacturing easily repeatable.

3. *Development and improvement of mechanical properties and complementary thermal analysis of PLA with percentages of VINNEX® ranging from 5 to 20% through injected samples.*

VINNEX®'s qualities are already declared by Wacker company. Nevertheless, the investigation focuses on possible improvement in PLA's rigidity characteristic. VINNEX® 2504 should be blended with different bioplastics in various percentages. The interaction between VINNEX® powder and PLA's granules gives flexibility to polymer's chain, resulting in more elastic material. However, it has not been selected which is the better ratio among studied. For sure, the increasing ratio of additive enhances PLA's mechanical properties. From TGA analysis, VINNEX® shows a degradation temperature lower than that of pure PLA. Consequentially this can result as an accelerated degradation process. Wacker states the totally compostability of its products, giving them adding values.

4. *Comparison between biopolymers' blends with and without addition of 10% VINNEX®.*

Since VINNEX® evidences great improvement in mechanical properties, it is meaningful investigate its addiction to other biopolymers' blends. To constant amount of 60% PLA and 40% of other bioplastics, was included 10% of additive. VINNEX® has the same positive effect on blends, as shown with pure PLA. New biopolymers' blends were subjected to same test as the previous ones. Comparison have revealed discordant results in compatibility. The possible compatibility between raw PLA and TPS, disappears by adding VINNEX®. The DSC curve shows two distinct peaks which stand for Tm of respectively both materials. Mechanical tests have been performed on density and hardness. The tertiary blends present heterogeneity conformation. In fact, the great mobility of VINNEX®'s chain permits to additive being involved in the matrix structure while donating flexibility to blends.

7.1. Work’s conclusion

The treatment carried out in the previous chapters highlighted the possibility to improve qualities and characteristics of bioplastics materials. Biopolymers are distinguished based on their structure, origin, end of life and their chemical and mechanical behaviour. These variety have to be considered in order to make bioplastic materials products competitive in the market. Despite the growing market interest in biopolymers there is still some lacks and confusion. This can produce misunderstandings and consequently mistakes in the commercial prospective from both legislative and applications point of views. For this reason, definitions in the present work have the aim to explain how big the bioplastics’ sector is and clarify some misleading concepts too. In AIJU’s laboratories all the tests were performed corresponding to the current legislation. When materials are subjected to tests, regulations issued by official bodies (ISO, ASTM, UNI) must be respected. The regulations specify the type of equipment to be used, how the specimens must be conditioned before the test and during it, to obtain validated results to analyse. Basically, the mechanical characterization carried out with different tests has wants to make understand whether biopolymers can replace the corresponding polymers in the manufacture of toys and other disposable applications. All the materials used have also undergone thermal treatments to evaluate the changes in properties following different processing methods, and possible the aging.

In the work, the experimental tests were focused on thermal and mechanical characterization. The thermal analysis is often the starting point in the analysis of the mechanical properties of materials. The combination of both analysis allow to obtain a wealth of information that can be used in further development of studies. The results obtained among all the thermal analysis show that PLA and TPS blends seem to be compatible in different percentages ranging from a minimum of 20 to maximum of 80%. While for the other biopolymers’ blends not significant compatibility is presented.

Peculiar focuses have been developed in PLA. As this material has many advantages, further improvement in its weakness are object of study. Its rigidity is translated in fragility when material is processed. PLA’s fragility results particularly in correspondence with high processing temperature and stress. The specimens show visible degradation and facility to break. During the tests, PLA’s specimens break at deformation values lower than when the test must be completed. This effect should not be overlooked if the material is used to make applications subjected to high stresses. Working on the results, the presence of more flexible materials has been tested.

As regarding mechanical behaviour, the addition of BioPBS and the additive VINNEX® give more flexibility to blends comparing to raw materials. Therefore, if in some applications a good ductility or flexibility is required, it is preferable to use these two compounds. Moreover, they show great processability that means to not change the conventional plastic equipment. At working temperature, BioPBS and VINNEX® do not seem to be affected by different temperatures treatments. Further observations should be made regarding the fact that for both materials greater improvements in blends follow the increasing amount. However, it is possible a saturation in content that leads to stop the enhanced rubbery state. If BioPBS is totally renewable and biodegradable, the same thing does not concern VINNEX®. In fact, it is a Vac-E and even Wacker declares its compostability, further investigation should be developed. Studying thermal behaviour, it is important to state that the degradation starts earlier for VINNEX® than for raw PLA. Considerations on degradation's temperature are important to future studies on biodegradability by UV, humidity (action of water, sunlight which in general can compromise the performance of any material).

7.2. Future prospective

Sustainability of products is becoming more important. Manufactures, retailers and buyers need to respond to this growing issue in order to remain relevant and competitive among the stakeholders about environment surges. Nowadays sustainability is a market's demand and the shift to ecommerce is invoking to explore ways to reduce packing too. Among the industries, toy sector is moving in sustainable direction. There are great examples of toy producers using recycled or bioplastics materials in either product or its packaging. Some brands are reducing use of synthetic plastics by replacing them with biobased materials, additive and colorants of natural origin. However, benefits that sustainability can bring to toy sector are challenging, because many restrictions in legislations and regulations must be accomplished. Ever more toymakers are exploring options for using more sustainable materials while respecting quality and compliance of products. Designing toys that will not break is an important commitment in term of safety. In fact, many researches are addressing attention in finding alternative to flexibility given by synthetic compounds.

Bioplastics give toy manufactures a degree of flexibility and chance for creativity that are lacking with traditional plastic formulations. However, the prices are still too prohibitive for lot of companies. The chemical industry's mission is creating an ideal material which has rubberlike behaviour, is both made from renewable resources as well as recyclable at the end of life and ensures a large enough volume quantity. These qualities should satisfy the demand and consumer's needs in toy sector: quality and safety's performance at economically viable too.

There is the urgency to expand researches on developing biomaterials that combine durability and versatility in uses. As the market is constantly increasing, continually researches are necessary to explore as many possible alternatives with improved benefits.

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