Treball de Fi de Grau

Grau en Tecnologies Industrials

Environmental Impact of Bioplastic Blends

MEMÒRIA I ANNEXES

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Abstract

Since the enormous and growing demand of plastics is a reality, the importance of the sustainability of these products is essential to the environmental conservation, from its very origin to its degradation, going through its manufacturing process. As common plastics (petro-based polymers) are made from fuel fossils, their production actively contributes to the carbon dioxide emissions, aggravating climate change.

In this scenario, biobased polymers (bioplastics) seem to be eco-friendlier alternatives that will be consolidating its place in the market. In the recent years, many research and development resources have been invested in this field. But a biobased polymer is instantly better for the environment than its petroleum based alternative? How do we compare the impact of these two?

The present project centers on the Life Cycle Assessment (LCA) of the production of REX-PLA (polylactide acid modified by reactive extrusion) done in a pilot plant. Furthermore, it assesses the impact and sustainability of industrial interest blends of REX-PLA with other polymers – in particular with acrylonitrile butadiene styrene (ABS) and two biobased polyamides (bio-PAs): PA 610 and PA 1010.

Once described the theoretical foundations to understand the project, the methodology involves selecting and computing different sustainability and environmental impact indicators to assess the environmental effect for the transformation processes done to the different blends. Afterwards, adding up the eco-profiles (cradle-to-gate LCA) of the materials to these results, it is possible to compare the total environmental impact of the different industrial interest blends with its origin polymer (ABS, PA 610 or PA 1010) to determine if, from an environmental point of view, it is worth the production of these blends in larger scales.

In the case of REX-PLA/ABS blend, transformation processes done in the pilot plant, turn into a greater impact for the environment than ABS alone, which proves that it is essential to integrate LCA practice throughout the development of environmentally friendlier products. On the contrary, both biobased polyamides blends with REX-PLA are found to be significantly ecologically-friendlier than the respective polyamides alone. In particular, a kilogram (kg) of REX-PLA/PA 610 blend requires 32.7 % less water and 24.5 % less energy to be produced than a kg of PA 610; and a kg of REX-PLA/PA 1010 blend requires 26.9 % less water and 41.4 % less energy to be produced than a kg of PA 1010.

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1. Glossary

Abbreviations and Acronyms

ABS	*Acrylonitrile butadiene styrene*
ABS-g-MAH	*Acrylonitrile Butadiene Styrene maleic anhydride grafted acid*
BF	*Biobased Feedstock*
CCP	*Centre Català del Plàstic*
CO_2	*Carbon dioxide*
EI’99	*Eco-Indicator ‘99*
GWP	*Global Warming Potential*
LCA	*Life Cycle Assessment*
LCI	*Life Cycle Inventory*
MINECO	*Ministerio de Economía y Competitividad*
PA	*Polyamide*
PLA	*Polylactic Acid*
PLLA	*Poly-L-lactide*
REX-PLA	*Reactive Extrusion modified Polylactic Acid*
SAmfE	*Styrene-Scrylic multi-functional-Epoxide*
ROP	*Ring-opening polymerization*
UV	*Ultraviolet light*

Units

° C	*degrees Celsius*
dm^3	*cubic decimetres*
kg	*kilogram*
kPa	*kilopascals*
MJ	*megajoule*
mmHg	*milliliters of Mercury*
mPt	*Eco-indicator millipoint*

2. Preface

2.1. Origin of the project

Today, one of the most relevant and worrying global concerning is the environment. We have proven physical evidences that climate change is a reality, and greenhouse gas emissions are one of the anthropogenic factors that more contributes to accelerate it. In particular, the increase in CO_2 levels due to emissions from fossil fuel combustion is distressing. Common plastics (petro-based polymers) are derived from petroleum or natural gas, helping to worsen this situation. Nevertheless, an eco-friendlier alternative is achieving importance in the market: bioplastics.

Bioplastics are biobased polymers, meaning that they must be derived from renewable biomass sources (such as vegetable fats and oils or corn starch) and/or biodegradable. Production of such plastics tends to require less fossil fuels and to produce less greenhouse gases than the production of common plastics. But the term bioplastics itself is often misleading to confusion, because it may suggest that any polymer derived from biomass or biodegradable is environmentally friendlier than conventional non-biodegradable plastics. The magnitude of the different biobased polymers environmental impact will depend on multiple factors, such as its type, manufacturing process, ease of recycling, etc.

2.2. Aim of the project

The aim of this project is precisely to determine whether productions of some particular biobased plastic blends are environmentally friendlier than their common plastic equivalent. In order to achieve that objective, it is essential to make a Life Cycle Assessment (LCA).

2.3. Scope of the project

The scope of the project is to realize an experimental gate-to-gate analysis LCA of a polymer transformation. The process studied includes the production of REX-PLA by reactive extrusion of PLA, and blending with other polymers (ABS and bio-PAs). To complement this analysis, the study will also include the theoretical bases to understand the project (an introduction of plastics and the environment, a recollection of the principal environmental impact and sustainability indicators, and theory on LCA) and cradle-to-gate LCA results of the base polymers to add-on to the gate-to-gate analysis, and determine the global sustainability of the blends.

3. Objectives

3.1. General Objective

The main objective of this project is to determine the sustainability and environmental impact of the “REX” (reactive extrusion) modification – and blending processes with other polymers – of PLA that is done in the *Centre Català del Plàstic* (CCP). This final degree project is part of the MAT2013-40730-P project, financed by the MINECO (*Ministerio de Economía y Competitividad*).

3.2. Specific Objectives

Beyond the general objective of this project, there are also some specific side objectives that will be pursued:

1. Introduce the importance of plastics in today’s society and highlight the priority to make them sustainable.
2. Introduce the primary applications and general characteristics of the PLA and explain the REX-PLA modification.
3. Describe the most relevant environmental impact quantifying indicators.
4. Describe the most relevant sustainability indicators.
5. Make a cradle-to-gate LCA of the studied blends, formed by the gate-to-gate LCA considered and researched eco-profiles (cradle-to-factory-gate LCA) of the base polymers.
6. Compare the results in this environmental assessment of the different blends to its origin polymers, to consider if it worth the production of any of these blends in a larger industrial scale.

4. Plastics and the environment

Due to their relatively low cost, ease of manufacture and versatility, plastics are used in an enormous and expanding range of products. Surprisingly, plastics can be found in packaging, clothing, toys, cars and spaceships. See figure 4-1 for the European plastics demand by segment in 2013.

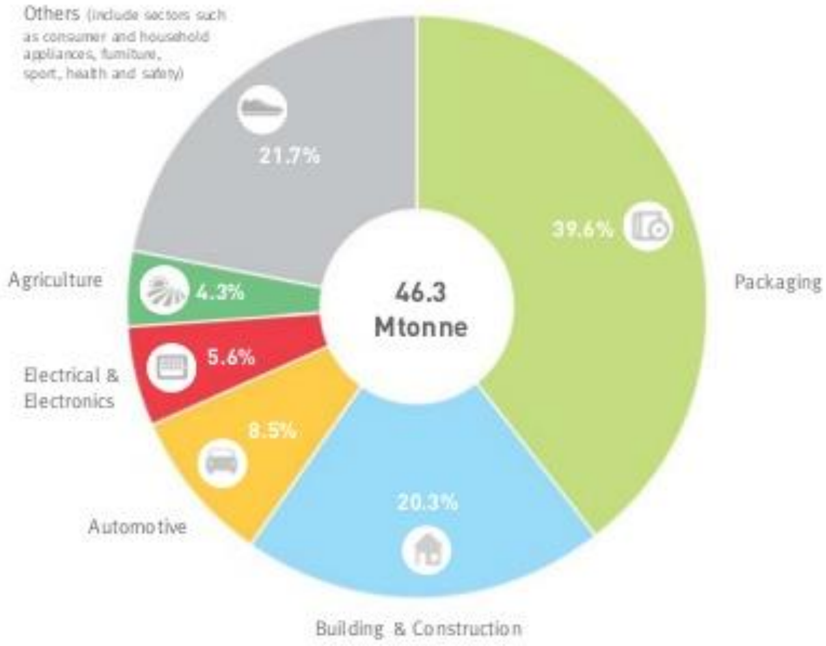


Figure 4-1: European plastics demand by segment in 2013 in millions of tones [1]

Plastics have already displaced many traditional materials, such as wood, stone, leather, paper, metal, glass and ceramic, in most of their former uses. Plastics are part of the daily life of people and their demand is constantly rising.

In comparison to other materials, plastics are relatively new. Its development has evolved from the use of natural plastic materials in the middle age, to the use of chemically modified about two centuries ago and finally to completely synthetic molecules, about a century ago.

Parkesine is considered as the first semi-synthetic plastic. It was patented by Alexander Parkes, in Birmingham, UK in 1856. Parkesine was made from cellulose (the major component of plant cell walls) and treated with nitric acid as a solvent. It would not be until the early 1900s when it was developed the first fully synthetic plastic, Bakelite, reported by Belgian chemist Leo Baekeland by using phenol and formaldehyde.

In the following years, the chemical industries developed a rising interest on polymers. In the 1930s, the first petro-based polymers were synthesized, including polystyrene (PS) and polyvinyl chloride (PVC). In the 1940s and 1950s this tendency outgrew: a wide range of new forms of plastics were created, such as Polypropylene (PP) and Polyethylene terephthalate (PET).

Since that moment, the demand on synthetic plastics has constantly grown. In the below figure 4-2 can be seen the global increasing trend in plastic production, from 1950 to 2014. However, in the EU we can see a maintenance trend after the 2008 crisis.

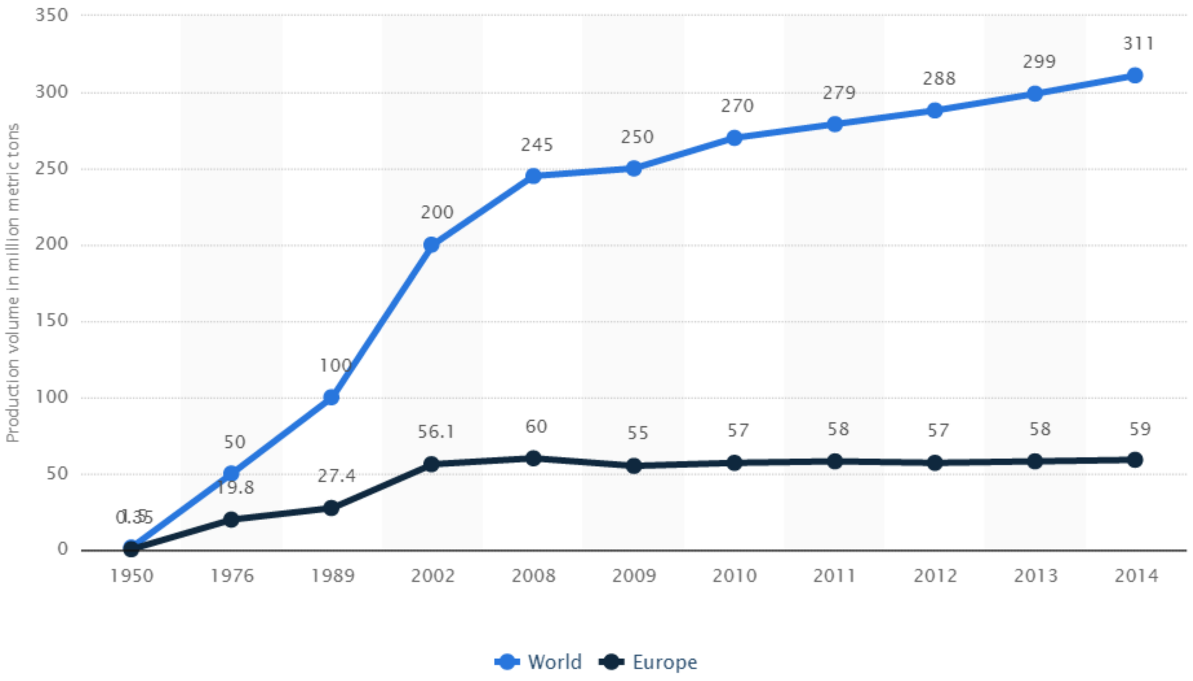


Figure 4-2 World and European plastics production progression [2]

As it has been shown, plastics are a wide and diverse industry. Recently, the enormous consumption of plastic, added to the concern in the environmental impact and resources conservation, obviates the need of a mentality change, towards a more sustainable industry. One of the most problematic aspects of polymer production is its raw material. As remarked before, common plastics are polymers made of petroleum, a non-renewable resource. Another issue to consider is the energy source used in the manufacturing process. Last aspect to take into account is the recycling process. Therefore, we must consider these three key factors in our model to determine whether a plastic is environmentally friendly or not.

For the first factor, raw material, there is an alternative to pretrobased plastics: biobased plastics, which are derived from biomass. In the following figure 4-3, can be appreciated the global production capacity of bioplastics by market segment in 2014.

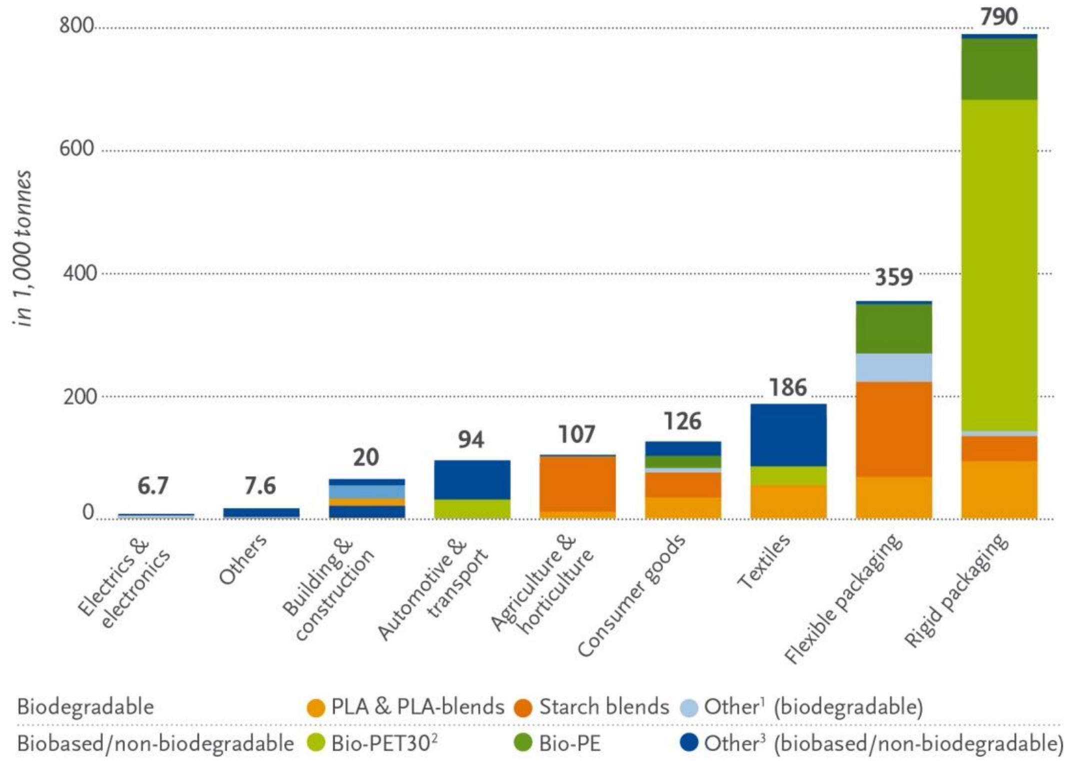


Figure 4-3: Global production capacities of bioplastics by market segment, in thousands of tones [1]

The manufacturing process sustainability (use of energy, water, emissions of CO_2, etc.) can be analyzed with Life Cycle Assessment tools, which will be covered in forthcoming sections. The other problematic aspect of plastics is the waste production. As plastics use to be non-biodegradable, they are very harmful to the environment and all the animal species. By instance, waste thrown to the ocean may trap or be ingested by marine animals.

When a plastic product arrives at the end of life, we can differentiate three main possibilities: recycle it, use it for energy recovery, or throw it to the landfill. Obviously, the first two options are preferred over the third. Furthermore, it is always preferred recycling the plastic when it is possible and the energy recovery option is the best for hard recycling plastics.

As we can see in the below graphic (figure 4-4), from 2006 to 2012, recycling and energy recovery routes have significantly increased, as the dumping choice had a decreasing tendency.

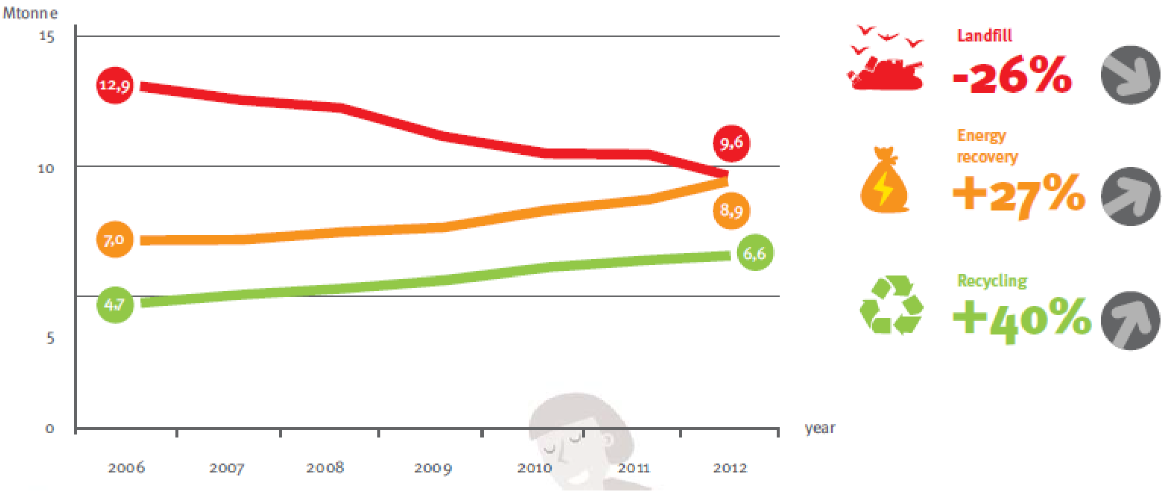


Figure 4-4: Plastic waste recycling and recovery, in millions of tonnes 2006-2012 [1]

It is essential to maintain this decrease trend of the percentage of plastic waste that is thrown into the landfill. In recent years, population is becoming more aware of this factor, allowing making a more efficient waste generation management.

Plastics have extraordinary properties and are suitable for a wide range of applications, at a relatively low cost. The Plastic industry is a pillar of the world economy and society, so it must be consistent with a sustainable development.

4.1. Bioplastics

As clarified in the previous section, plastics are essential to the daily life of the population, and its market is still expanding. However, common plastics have some important issues to be considered:

- Plastics may be of one single use.
- Fossil fuels are finite and its price is volatile.
- They actively contribute to the environmental contamination.

For all the above reasons, biopolymers (commonly known as bioplastics) could be legitimate alternatives for a more sustainable development.

Bioplastics are a wide family of products – based on plants – that differ on properties and applications for a vast category of sectors, such as Packaging, Agriculture, Electronics, Textiles and Medical. The bioplastic definition of the *European Bioplastics* agency includes plastics whose raw material is biobased or/and biodegradable. In figure 4-5 is shown how the biopolymers family is divided into three of the four possible quadrants [3]

- Plastics with biobased raw material but non-biodegradable.
- Plastics with biobased raw material and biodegradable.
- Plastics with conventional raw material but biodegradable.

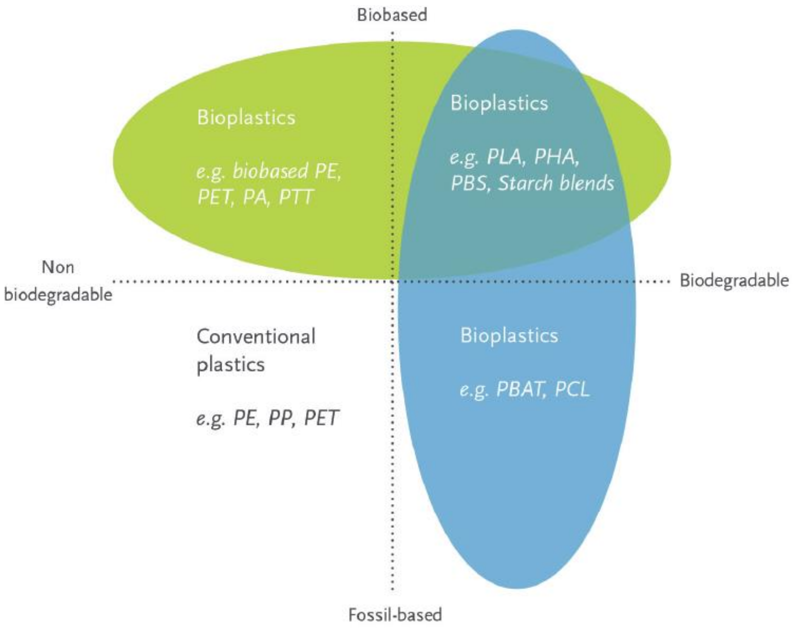


Figure 4-5: Types of plastics [3]

4.2. PLA

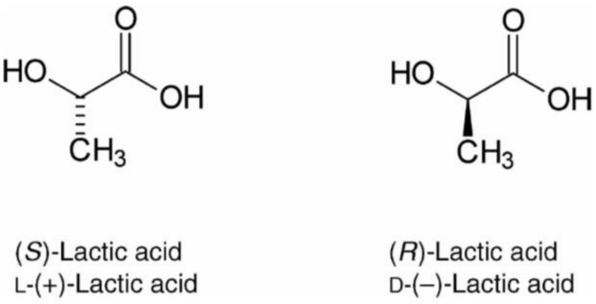
Polylactic acid or polylactide (PLA) is a biodegradable aliphatic thermoplastic polyester derived from renewable resources, such as corn or sugarcane. PLA has a similar behaviour to PET (Polyethylene terephthalate), which is why it is widely used for diverse applications. In fact, in 2010 PLA had the second highest consumption volume of any bioplastic of the world [4].

4.2.1. History

Polylactic Acid was first discovered in 1845 when Theópile-Jules Pelouze condensed lactic acid through a distillation process of water to form low-molecular-weight PLA, but polycondensation process merely produces low purity PLA. Almost a century later, Wallace Carothers found that the heating of lactide in a vacuum produced PLA. However, this process was not feasible on an industrial scale due to the high cost of purification. In 1997, Cargill and Dow Chemical created a joint venture named Cargill Dow Polymer LLC to further commercialize PLA. They succeed and introduced in the market their new products. [5]

4.2.2. Structure

Lactic acid, which is the feedstock for PLA, has two enantiomers (Figure 4-6) and is considered both biodegradable and biobased.



(*S*)-Lactic acid
L-(+)-Lactic acid

(*R*)-Lactic acid
D-(–)-Lactic acid

Figure 4-6: Lactic acid enantiomers [5]

Although both enantiomers are attainable, on industrial scale it is easier to obtain the L-isomer. Consequently, commercial grades of PLA will be homo-polymers formed by L-enantiomers (PLLA) and co-polymers.

The isomer ratio in a PLA grade influences in its processability, degradability and crystallinity. Copolymers present less crystallinity and a lower melting temperature [6]. For that reason, homo-polymers, like PLLA, must be processed at high temperatures (above 180 ºC), at which suffers a significant degradation [7].

4.2.3. Manufacturing process

Nowadays, there are three principal routes to produce PLA polymers from lactic acid, as it can be appreciated in figure 4-7. However, as it has been said, direct polycondensation can merely form low molecular weight PLA. Therefore, producers have two main industrial routes to obtain usable (i.e. high molecular weight) PLA: ring-opening polymerization of lactide with various metal catalysts, and polycondensation by connecting carboxyl and hydroxyl groups.

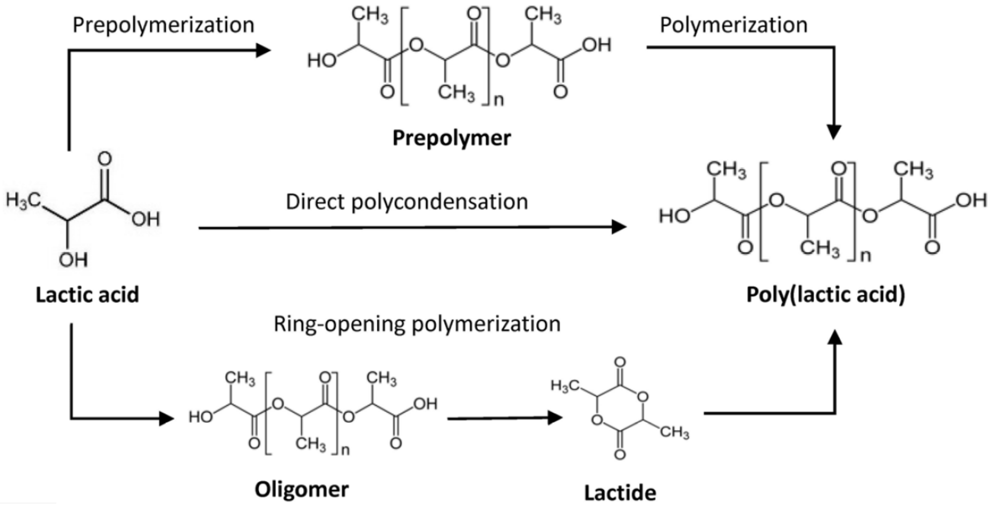


Figure 4-7: Routes of poly(lactic acid) (PLA) synthesis from lactic acid [8]

While the former technique requires severe conditions in order to obtain a high-molecular-weight polymer, the latter method can afford a high-molecular-weight PLA with narrow molecular weight distribution at relatively mild reaction conditions [6]. Consequently, ring-opening polymerization of L-lactide is the most common route adopted in the ordinary industrial production of poly(L-lactic acid). In table 4-1 can be differentiated process conditions for both methods.

	Method	
Reaction Conditions	**Direct condensation**	**Ring-opening polymerization**
Temperature (ºC)	High (180-200)	Moderate (130)
Pressure (mmHg)	Very low (5)	low (1875)
Reaction times	Long	Short

Table 4-1: Direct condensation of lactic acid monomers and ring-opening polymerization average conditions; adapted from [6]

Many authors suggest different parameters in order to obtain high purity PLA. A proposed way by *Sanglard et al* [5] can be appreciated on figure 4-8.

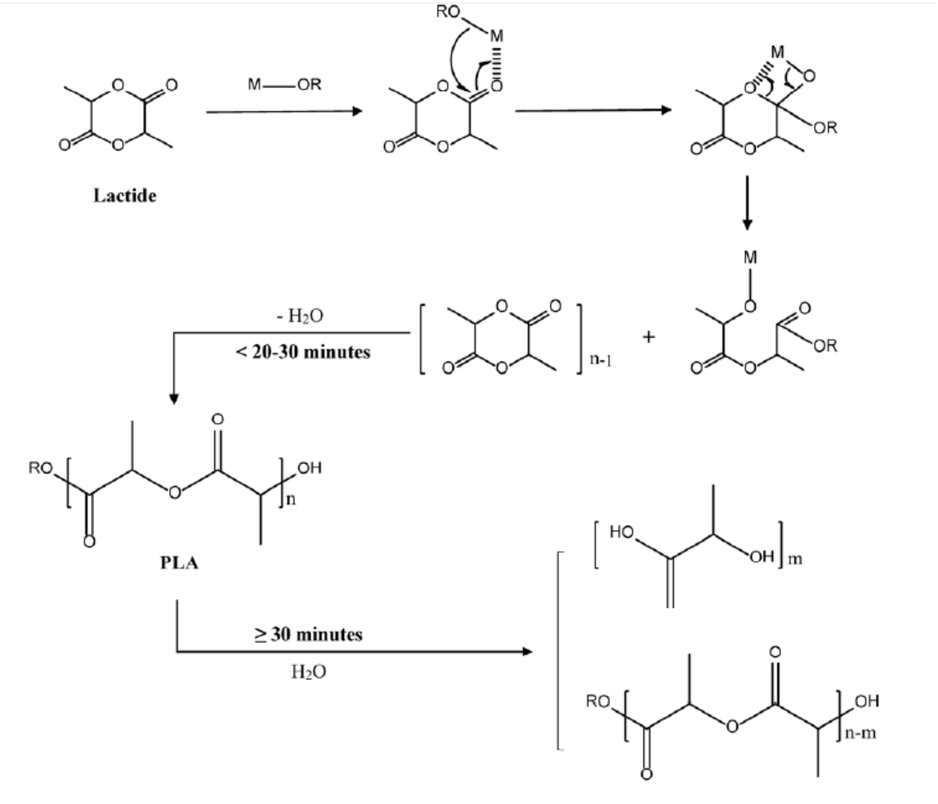


Figure 4-8: Proposed scheme for ROP [5]

When usable PLA is obtained by one or another route, even higher molecular weights can be attained by carefully crystallizing the crude polymer from the melt [7].

4.2.4. Properties and applications

PLA possesses similar properties to traditional hydrocarbons based polymers, but with the added advantage of coming from renewable sources and the possibility of being biodegradable. Thus, it has good biocompatibility, which makes it really useful for biomedical applications. It is quite transparent, brilliant and it is possible to obtain a satisfactory surface texture. It is also rigid and versatile for processing. Therefore, it is a fair candidate to substitute traditional thermoplastics such as PET or PS in multitude of industrial areas, like packaging, textile or medical sectors, as it can be seen in figure 4-9.

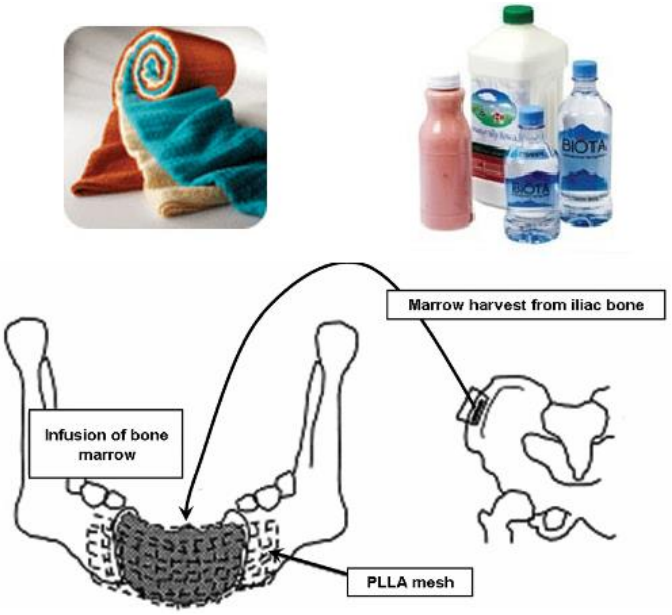


Figure 4-9: Different PLA applications: textile, packaging and medical; adapted from [5]

All these traits make PLA an extraordinary interesting material. Therefore, PLA production optimization is an actual important source research. However, despite its mechanical properties are comparable to traditional thermoplastics and would be suitable for the mentioned applications, its thermic properties are not so satisfying. It has a low glass transition temperature of 60 ºC and suffers different degradation issues, especially critics above 200 ºC [7]. Consequently, it is required to adopt strategies to avoid or palliate these degradation mechanisms. In fact, scientific efforts in the field, has increasingly focused on transformations of PLA above all polymer modifications (figure 4-10).

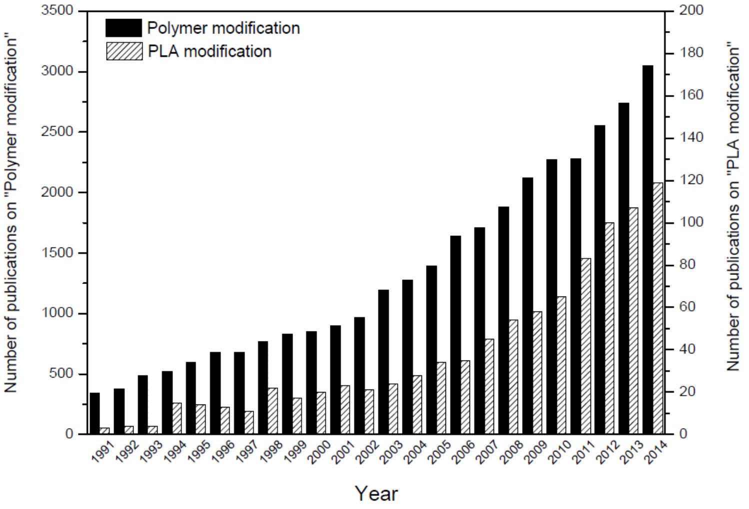


Figure 4-10: Number of publications with key terms "Polymer modification" or "PLA modification" in the period of 1991 to 2014 [8]

4.2.5. REX-PLA

A particular way to modify PLA is through reactive extrusion, and the structurally modified polymer is consequently named as REX-PLA. In the reactive extrusion process degradation behaviour of PLA is improved as consequence of an increase of molecular mass. In the process, some specific reactions are favoured by the reactivity provided by the chain extending agent [9]. These reactions counteract the polymer degradation processes. This results in a PLA with less sensitivity to temperature and melting improved behaviour.

4.2.5.1. Reactive Extrusion

Taking a further look on the insights of reactive extrusion may lead us to a better understanding of REX-PLA. Reactive extrusion presents several advantages on discontinuous reactors in the polymer structural modification field. The most important one is that it allows unifying in one single step production and processing of materials. This is possible because in the process they are combined simultaneously heat and mass transport operations of a natural extrusion all along with the chemical reactions that grant modifying polymer properties. In particular, in the bio-polymers scope, this technique is useful since it provides a more inexpensive and effective way to improve the principal weaknesses of using biodegradable polymers and renewable source plastics: its sensitivity to degradation and thermo-mechanical properties [9].

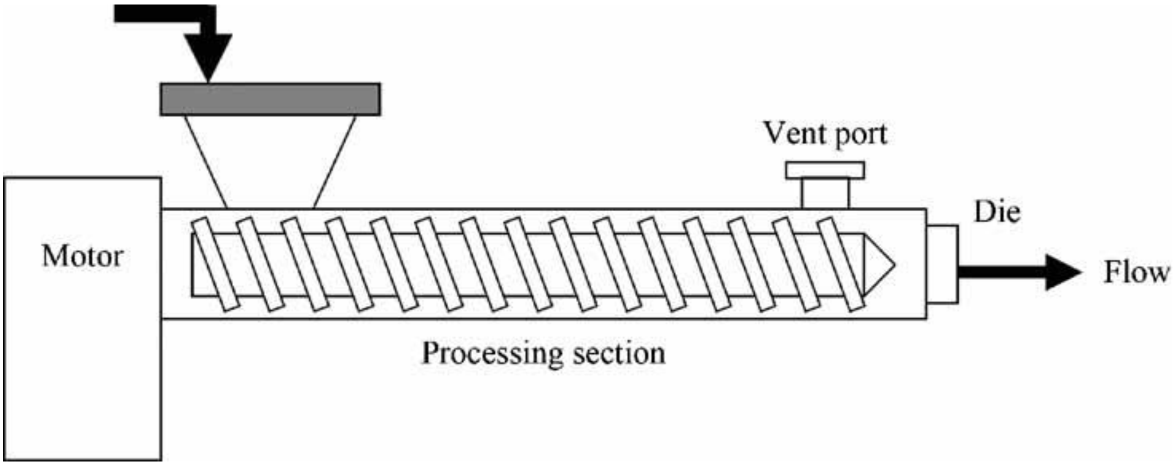


Figure 4-11: Scheme of a polymer extruder; adapted from [7]

Furthermore, reactive extrusion is a process that enables to exhaustively control the materials residence time, allowing a fine homogenisation of components and the possibility of adding the reactants in different stages. Hence, we can obtain the precise desired material specifications through the die.

As, in general, residence time necessary to complete all the chemical reactions is lower than in most reactors, exposition time of polymers at high temperature – which may lead to early degradation – is reduced. Another benefit of this technique is that extruders might work with high viscosity materials without the call for adding solvents, allowing substantial savings in recovery, raw materials and cost of this equipment [9].

For the reactive extrusion process it is possible to use single or twin-screwed extruders. However, owe to the advantages of the latter ones, the twin-screwed type are widely used in this transformation. These categories of extruders allow an improved control of residence time, and enhanced heat and matter transfer capacities, making them adequate for homogenization, additives dispersion, polymerization and polymer binding purposes [10].

Extrusive reaction twin-screwed extruders can be divided in two sub-categories, according to the relative movement between the two screws: co-rotating and counter-rotating. The co-rotating variety has the advantage of not showing dead zones – where material could be isolated – as result of the spindles auto-cleaning effect [10]. Therefore, co-rotating twin-screwed extruders can work at higher speed, shear stress and production ratios.

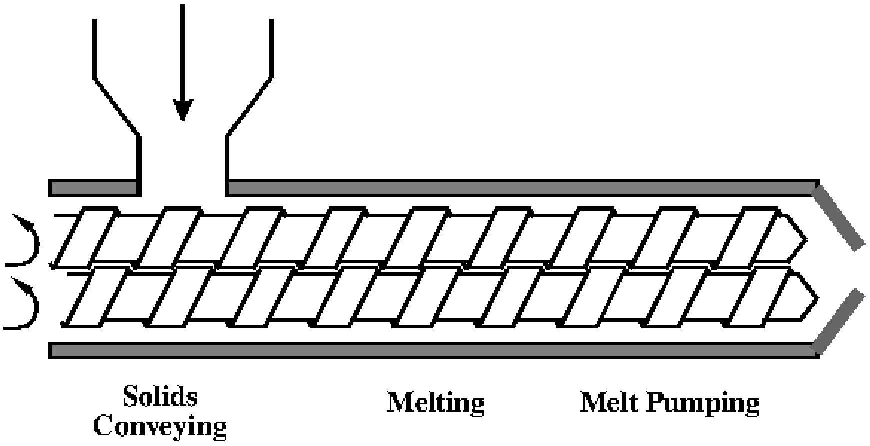


Figure 4-12: Scheme of a co-rotating twin-screwed extruder machine [11]

For all the reasons stated above, a co-rotating twin-screwed extruder – shown in figure 4-12 – will be used for the first sept of the polylactic acid transformation: extrusive reaction to produce REX-PLA and enhance the PLA properties. During this process, a chain extending agent is used in order to preventing PLA degradation.

4.2.5.2. Degradation mechanisms and chain extension reactions

On one hand, PLA is subject to thermal degradations above its melting temperature, especially during processing, leading to a reduction of the molecular weight and viscosity – the material properties deteriorate [9]. The degradation mechanisms are the following:

- The residual water inside the polymer matrix may activate hydrolysis reactions which split up the polymer chains (figure 4-13(a)).
- Backbiting effect (similar to depolymerisation – see figure 4-13(b)) leads to the formation of cyclic oligomers (lactide) and lactic acid.
- Intramolecular and intermolecular transesterification mechanisms – 4-13(c) and 5-7(d), respectively – could also cause a drop in molecular weight at longer reaction times.
- Finally, pyrolysis mechanisms (figure 4-13(b)) should also be considered (at high temperatures, i.e. above 300 ºC), where cis-elimination formats carboxylic acid groups and a polymer chain containing acryloyl groups [9].

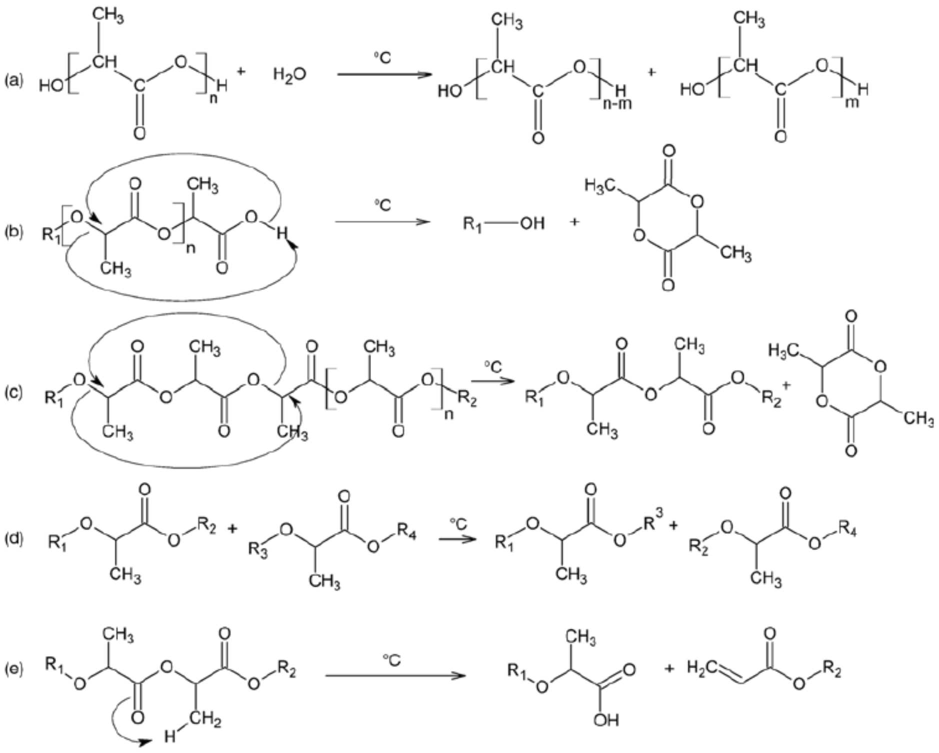


Figure 4-13: Degradation reaction of PLA: (a) hydrolysis; (b) backbiting; (c)intramolecular transesterification; (d) intermolecular transesterification; (e) pyrolytic cis-elimination [9]

On the other hand, in reactive extrusion these mechanisms are counteracted by the chemical reactions that take place with chain extension agents. Both polyester and groups carboxyl or hydroxyl groups can react with epoxy functional groups via ring-opening reactions. In a previous study done in CCP, SAmfE (Styrene-Acrylic multifunctional-Epoxide) was already used as an extending agent, in a reactive extrusion with PD,L-LA. In a first step, PD,L-LA carboxyl groups open SAmfE epoxy rings which results in grafting, followed by chain extension reactions, and finally n arms star formation [9] – as can be seen in figure 4-14. In a second step, and for longer reaction times, SAmfE's high reactivity may lead to comb or tree type structures; or even network structures if an excess of the extending agent occurs.

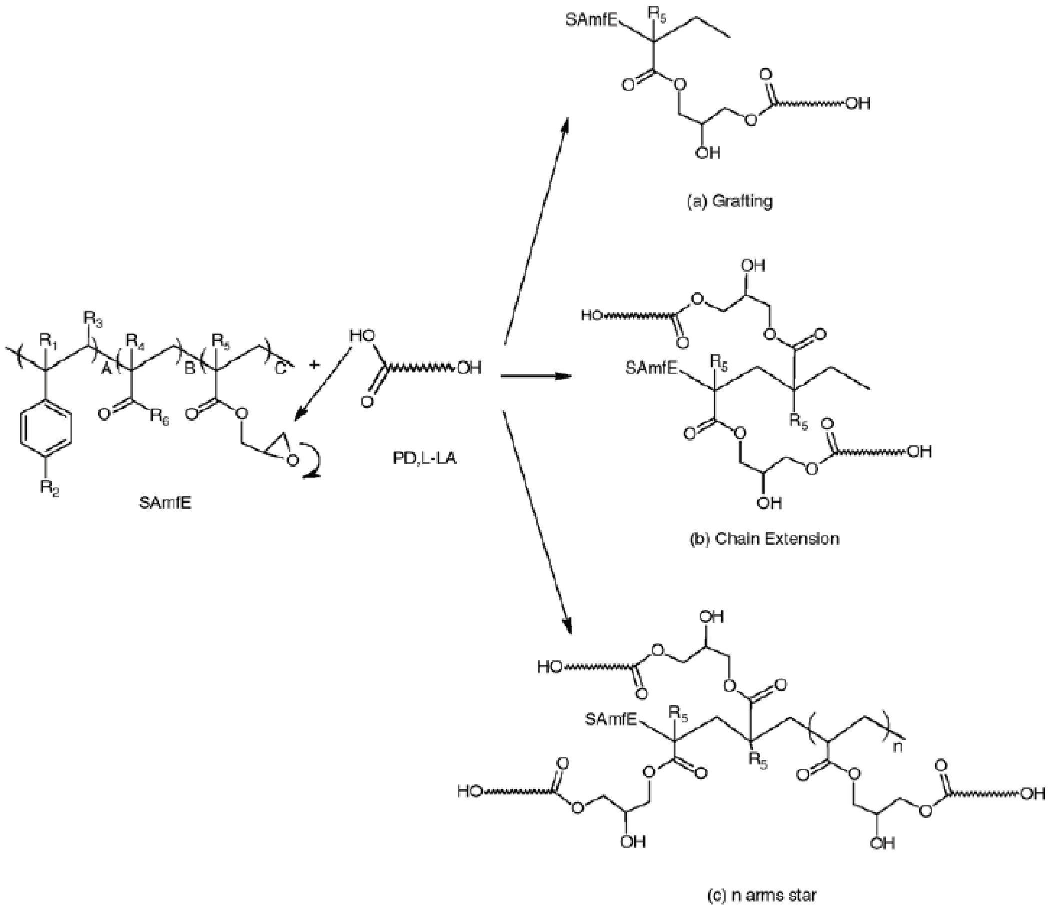


Figure 4-14: Possible reactions occurring by PD,L-LA and SAmfE agent: (a) grafting; (b) chain extension; (c) n arms star

Those two types of mechanisms (degradation and chain extension reactions) act simultaneously. Therefore, while length of aliphatic chains of PLA decreases due to degradation, the extending agent joins it again, allowing restoring the loss of properties of the PLA.

4.2.6. PLA Blends

A second strategy to improve PLA properties may be to blend with other thermoplastics. In the current project, the blends will be with acrylonitrile–butadiene–styrene (ABS) and polyamide (PA). This stage pretends to achieve a thermoplastic with similar properties to ABS (or PA) but with the environmental advantages of a bioplastic as PLA. If this alternative proves to be feasible and more sustainable than ABS (or PA), it would be a great improvement for many applications, drastically reducing environmental impact and ecological footprint associated to industrial processing.

The difficulty of this objective consists of solving the miscibility problem of biopolymers with industrial polymers. In particular, ABS and PLA blends show poor interfacial addition and heterogeneous morphologies (figure 4-15). This conditions turn into blends with low mechanical properties and bad thermal resistance [9]. The most widespread method to palliate this problem is introducing a compatibilizing agent in the blending process, which will generate the necessary interface for the correct matching of PLA and ABS phases.

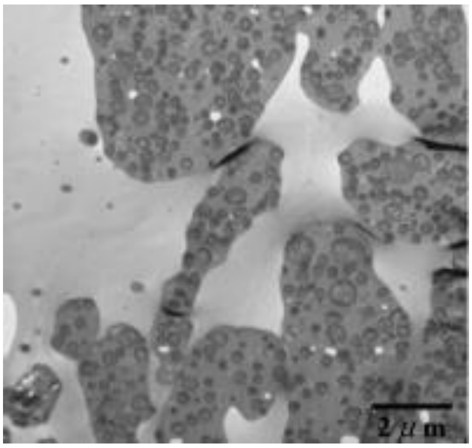


Figure 4-15: Transmission electron microscopy image of the immiscibility of PLLA and ABS; adapted from [5]

In this study, ABS grafted with maleic anhydride (ABS-g-MAH) has been chosen as compatibilizing agent. By introducing it in the mixture, interaction between maleic anhydride reactive groups present in the ABS-g-MAH and epoxy groups created in the reactive extrusion of PLA is achieved [7], resulting in a fine adherence between PLA and ABS.

In the case of PA, the subsequent application requires a polymer with the two differentiated phases, so there is no need for any compatibilizing agent.

4.3. Bio-PA

A polyamide (PA) is a macromolecule with repeating units linked by amide bonds, and may be synthetized both naturally and artificially. Synthetic polyamides are commonly used in textiles, automotive applications, carpets and sportswear due to their high durability and strength.

Figure 4-16: Different Polyamide applications

In most cases, they are crystalline thermoplastics characterized by a combination of methylene groups (CH_2) and amide groups -NH-CO- in their chain. The polyamides can be classified into two groups: AB-polyamides which consist of one basic unit or AA / BB-polyamides characterized by two basic units. In the case of PA, the term bio refers to their natural sources origins, but they are non–biodegradable (see section 4.1 for a better understanding).

Polyamides partly or totally biologically based can be produced using different processes, such as polycondensation of dicarboxylic acid diamide with water elimination, polycondensation of carboxylic acids as bifunctional monomers and ring open polymerization of the ε-Caprolactan ($C_6H_{11}NO$).

The polyamides used in this project experiments are: polyamide PA 610 and polyamide PA 1010, both manufactured from castor oil. In figure 4-17 can be seen the different types of PA obtained from castor oil, according to the process followed.

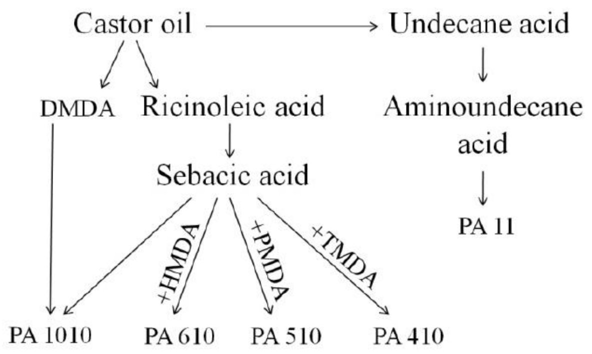
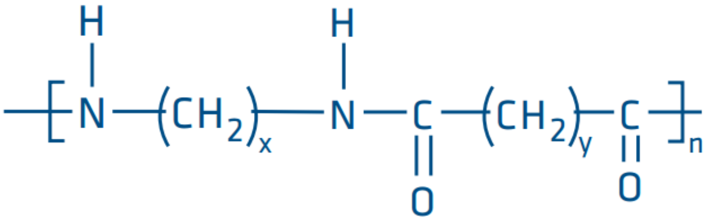


Figure 4-17: Main routes of manufacturing bio-polyamides from castor oil DMDA – decamethylenediamine, TDMA – tetramethylenediamine, PMDA – pentamethylenediamine, HDMA – hexamethylenediamine; adapted from [12]

The PA 610 can be obtained from a sebacic acid – which is obtained from castor oil (obtained by pressing the seed of castor plant or *Ricinus communis*). Therefore, the PA 610 is partially based on bio-renewable feedstock. Furthermore, it has high impact resistance at low temperatures, has low water absorption and is resistant to environmental exposure and very stable. It is a semi-crystalline polyamide commonly used in monofilament form in applications such as bristles and brushes.

PA 1010's feedstock monomers are decamethylene diamine and sebacic acid both obtained from castor oil. Hence, it is a polyamide whole based on bio-renewable resources. Its semi-crystalline structure provides for high mechanical strength and chemical stability. It absorbs little water, so its mechanical properties vary little when exposed to changing environmental humidity.

In the following figure 4-18 can be seen the chemical structure of PA having two source materials. Variables x and y in the figure are referring to the number of carbons in each monomer. In the specific case of PA 610 x is 6 and y is 8. Likewise, for PA 1010, x is 10 and y is 8.



$$-\!\left[\mathrm{NH}-(\mathrm{CH_2})_x-\mathrm{NH}-\mathrm{C(=O)}-(\mathrm{CH_2})_y-\mathrm{C(=O)}\right]_n-$$

Figure 4-18: Chemical structure of two source materials polyamide. Adapted from [12]

4.4. ABS

Acrylonitrile butadiene styrene (ABS) is an amorphous thermoplastic polymer extensively used in the plastic industry, being household products and consumer goods their major applications. ABS's light weight and ability to be injection molded and extruded make it useful in manufacturing products such as drain-waste-vent (DWV) pipe systems, musical instruments, automotive bumper bars, medical devices for blood access, and keyboard keycaps.

It is classified as styrenic copolymer since it is obtained by polymerizing styrene $(C_8H_8)_X$ with acrylonitrile $(C_3H_3N)_Z$ in the presence of butadiene $(C_4H_6)_y$. The proportions of each may vary, but are around 15 % to 35 % of the acrylonitrile phase, from 5 % to 30 % of the butadiene and from 40 % to 60 % of the styrene phase. In figure 4-19 the chemical structure of the main components of ABS are shown.

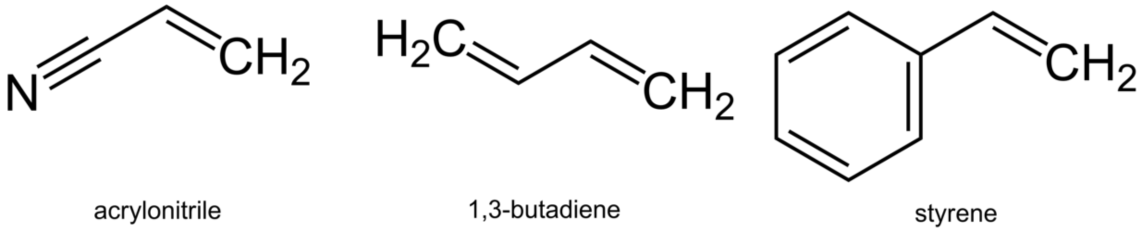


Figure 4-19: Chemical structure of the main components of ABS; adapted from [13]

The result is a ter-polymer of two-phase structure in which styrene and acrylonitrile form a continuous matrix, creating what is called as phase SAN (styrene-acrylonitrile resine) – and another phase which may be named internal phase, dispersed within the matrix formed by butadiene (figure 4-20 shows the representation of this structure). In fact, ABS can be explained as a SAN polymer where a butadiene phase – that acts similarly as an elastomeric impact modifier – is added. SAN phase is similar in properties to polystyrene: it is transparent, bright, and hard. It also has great stability, dimensional accuracy and a high elastic modulus, and allows obtaining high quality surface finishes. The acrylonitrile component gives excellent good heat resistance and toughness. On the contrary, its main drawback is its fragility. The phase butadiene solves this weak point, providing very good impact resistance and good toughness even at low temperatures.

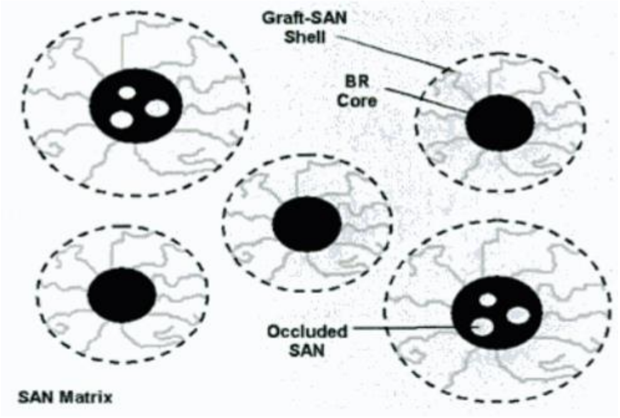


Figure 4-20: Schematic morphology of the two-phase system ABS (with SAN occlusions in the butadiene rubber elastomer phase) [13]

The properties of each grade of ABS will depend on the proportions of each monomer, enhancing in each case the required property. Morphology of the material and the level of interaction between the internal phase and the matrix are also essential. The relationship between the properties of ABS and its phases (butadiene and SAN) can be seen more clearly in figure 4-21.

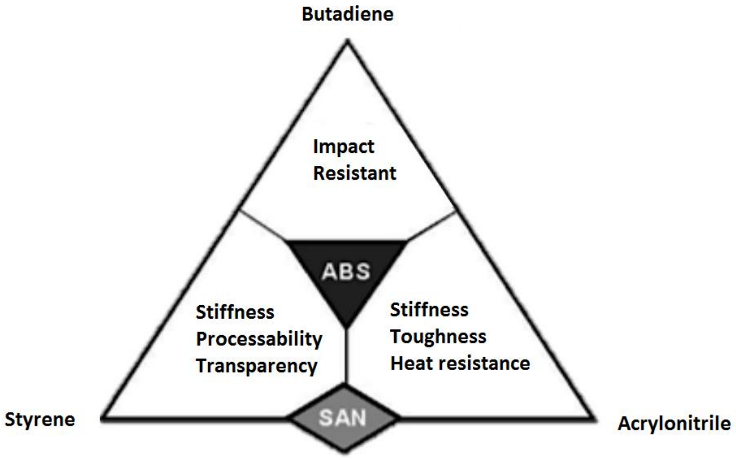


Figure 4-21: ABS phase properties contribution; adapted from [13]

Overall, ABS results in a versatile material, suitable for applications involving mechanical stress, good finishes, and thermal stability.

5. Environmental Indicators

An environmental indicator is a parameter used for quantifying and simplifying a phenomenon, and reflecting in a synthetically way a social concerning about the environment. Good environmental indicators are simple, clear, specific and representative in order to make worthy comparisons. The must have scientific ground, as well as noble reliability and be accessible to the general public.

The main objective of these indicators include facilitating decision making in environmental affairs, providing equivalent data on a national and international levels, and obtaining a systematic information which should guarantee an easy comprehension for non-experts [14].

Mainly, environmental indicators can be classified in two sub-categories: environmental impact indicators and sustainability indicators. Some indicators may fit into both categories, so they are defined as sustainability and impact environmental indicators.

5.1. Sustainability indicators

Sustainability is the capacity of any system of keeping active and productive in equal conditions all over time. Therefore, sustainable development involves being in harmony with biophysical systems and should aim to provide everyone the opportunity of living with the same quality of life. These indicators show the balance between resources recovery and irreversible changes in the environment.

5.1.1. Ecological Footprint

Ecological Footprint is defined as the area of ecologically productive land which is necessary to produce the used resources and assimilate the wastes originated, by a specific population and in a particular territory. Hence, ecological Footprint measures the supply and the demand on nature. Ecological Footprint may be obtained by dividing the average annual consumption per individual (kg/habitant) by the average annual productivity (kg/ha), and consequently is measured in relative surface units, more concretely, in hectares/person.

In the supply side of the equation, biocapacity represents the planet's biologically productive land areas (forests, pastures, cropland and fisheries). On the demand side, Ecological Footprint represents the productive area required by a population: an individual, city, nation, or the humankind. The productive area currently occupied by human infrastructure is also included in this calculation, since built-up land is not accessible for resource regeneration. Since the 1970s, humanity has been in ecological exceed with annual demand on resources being greater than what Earth can regenerate each year [15]. By measuring the Ecological Footprint we can assess our effect on the planet, which helps us take personal and collective action in preserving the environmental wealth.

Regarding the nature of the impact of human activities, Ecological Footprint can be disaggregated into six different types:

- Carbon Footprint: related to energy, it gives an equivalent to the theoretical area that is required to absorb the CO_2 emissions produced by the combustion of fossil fuels, chemical processes and changes in the soil uses. As this measure is usually given in kg of CO_2, it is required an equivalent factor to provide the footprint indicator in hectares.

- Pastures Footprint: calculated taking into account the pasture land consumed by the grazing animals.

- Fishing Footprint: computed from the marine surface required to obtain fish for consumption.

- Cropland Footprint: calculated from the area used to produce consumption or storage food, fiber and oils for humans and animals.

- Forestry Footprint: considered as the forest surface needed for the plantation of wood products.

- Urbanized land Footprint: estimated by area occupied by human infrastructures, including transport, households and industrial buildings.

In order to obtain an indicator with a single measure unit, equivalent and performance factors are applied to each of these measures. The former ones transform a specific land area in hectares to its equivalent of biologically productive area (global hectares), and the latter ones correct the differences between the production of a given land between different nations.

5.1.2. Global Warming Potential (GWP)

Global warming is defined as the increment in the mean earth temperature, primarily caused by greenhouse gases. As an excessive quantity of greenhouse gas is emitted to the atmosphere, the heat is trapped and climate change aggravate.

This greenhouse effect is contemplated by the Global Warming Potential (GWP). As a determined mass of carbon dioxide can trap a certain amount of heat, this indicator is measured in kg of CO_2 equivalent [14].

5.1.3. Required Material

It indicates the required material type and its quantity used to obtain a product. In this case, raw material also includes imported and exported material and this indicator unit is the kg.

5.1.4. Material subject to recycling

This indicator represents the potential of the used materials to be recycled at the end of the life of the product, giving a measure on the production efficiency, as well as a sustainability indicator. This indicator is given in kg.

5.1.5. Abiotic Depletion Potential

Abiotic resources are natural resources that are not considered living beings and yet are essential to human life, i.e. human exploited resources, such as fossil oil, solar energy or the iron mineral [14].

Therefore, this indicator measures the exhaustion of renewable and non-renewable resources. Bearing in mind there are many different methods and techniques for calculating this indicator, unit measures may vary from equivalent kg of Antimony to dimensionless.

5.2. Impact indicators

These indicators inform about the human activities on the environment, the implications of counter-producing actions for human health, life quality and the ecosystems integrity. Indicators are based upon quantitative or statistical measures of the environment conditions and may be used locally, regionally, nationally or globally.

5.2.1. Eco-indicator 99 (EI'99)

It is an indicator that provides precise information about the environmental impact of a product or process within the framework of the Life Cycle Assessment. Despite the complexity of the calculation method, it allows obtaining a single number indicative of a wide spectrum of environmental impacts. The following standards are taken into account:

- Materials: include the procedures needed for the material production, since the raw material is extracted until it is finished the elaboration of the product, including the transportation. Equipment goods, such as buildings and machinery are not included.

- Production processes: emissions in the process and energy generation required. Equipment goods are not included.

- Transports: includes highway, railway, marine and aerial transport for different loads. In this case equipment goods are included: road construction, railway infrastructures, etc.

- Generation of energy procedures and emissions, including energy conversion and fuel production.

- Processes to eliminate produced wastes, recycling and reducing the impact on the environment.

In theory, this indicator is dimensionless. However, in practice a standardised unit called the eco-points are regularly used as reference. One eco-point (Pt) is equivalent to a hundredth part of the annual environmental load of the average European citizen [16].

5.2.2. Greenhouse Gases (GHG)

The soil absorbs part of the energy received from the sun and irradiates the rest to the space. However, some gases, call greenhouse effect gases, absorb part of this irradiated energy and trap it into the atmosphere. Without greenhouse gases, the average temperature of Earth's surface would be about −18 °C (0 °F), rather than present average of 15 °C (59 °F). However, the recent increase on global consumption has leaded us to an excess of these types of gases, which turns into a global increase of the average temperature. This indicator focuses on emissions of gases that produce an increment of the greenhouse effect: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3), water vapor (H_2O) and Chlorofluorocarbons (CFCs) [17].

Figure 5-1 below shows a simplified representation of the contemporary global carbon cycle. Changes are measured in gigatons of carbon per year (GtC/y).

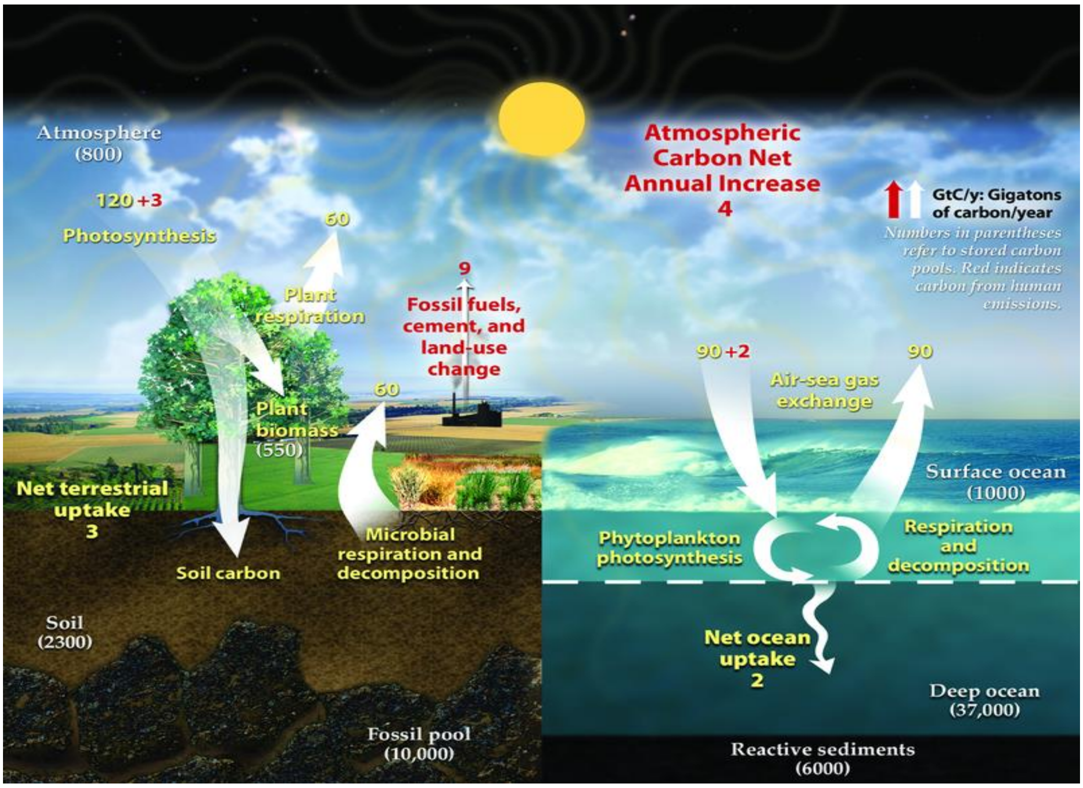


Figure 5-1: Influence of human emissions on the carbon cycle [18]

5.2.3. Ozone Depletion Potential (ODP)

The stratospheric layer creates a thin shield in the atmosphere, protecting the earth against ultraviolet light (UV). If a substance released into the air that contains chrome and brome molecules, such as trichlorofluoromethane (CFC-11) or Chlorodifluoromethane (R-22), it threatens to degrade this layer [14]. The result of this phenomenon is known as the Ozone Hole. The ODP indicator relates the impact of an activity or process in the Ozone Layer, and it is quantified in kg of equivalent CFC-11.

5.2.4. Eutrophication Potential

Eutrophication or hypertrophication is the ecosystem's response to the addition of artificial or natural macronutrients, mainly phosphates and nitrogen, through detergents, fertilizers, or sewage, to an aquatic system [19]. Therefore, there is a massive proliferation in seaweed that incites an oxygen deficit. The absence of the oxygen decreases biodiversity because many microorganisms that need die, and may also muddy and putrefy water. Eutrophication Potential is measured in kg of equivalent phosphate.

5.2.5. Acidification Potential

Acidification potential quantifies the environmental impact of human activities that cause acidifying substances, for instance CO_2, SO_2, NO_X and NH_X, in marine ecosystems, including surface water and subsoil. Acidifying substances increase the hydrogen ion concentration, which turns into a decrease in the pH levels [20]. Therefore, chemical balance is lost, so biodiversity of species is threatened. This potential is measured in kg of equivalent SO_2.

5.2.6. Human Toxicity Potential (HTP)

Toxicity is the capacity that a substance has to be poisonous or harmful to a life being when there is contact. As some substances may be more harmful in different environments, there can be distinguished different types of toxicity: human health, terrestrial and aquatic toxicity.

Human Toxicity Potential (HTP) reflects the potential harm of a unit of chemical released into the environment, and is based on both the inherent toxicity of a compound and its potential dose [21]. Total emissions can be evaluated in terms of kg of equivalent benzene. It is worth to highlight that for the human health indicator type, some studies differentiate if the toxic substances are carcinogens or non-carcinogens. In this case, terms of equivalent benzene are used for carcinogen emissions and equivalent toluene for non-carcinogens.

5.2.7. Photochemical Smog

Photochemical smog is the chemical reaction of sunlight, nitrogen oxides and volatile organic compounds (VOC) in the atmosphere, which leaves airborne particles and ground-level ozone [22]. These VOC are the primary pollutant – directly emitted from the source – but also secondary pollutants are created in reactions with ultraviolet light, such as hydrocarbons, nitrogen hydroxide. The capacity of a system of producing photochemical smog is quantified by an indicator using as reference units the kg of equivalent ethylene.

Figure 5-2: Photochemical smog in the Barcelona metropolitan area

5.2.8. Respiratory effects of organic and inorganic compounds

In the last decades, the increase in the industrial activity has amplified the emissions of organic and inorganic particles. Breathing this contaminated air may turn into serious health problems to humans, like asthma, cardiovascular diseases and even premature death. Respiratory effects of organic compounds are measured in kg of equivalent ethylene.

5.2.9. Wastes associated to production

In every productive process, wastes are generated. These wastes must be transported, evaluated and treated for reutilization, incineration or disposed in dumpsters. As these wastes, toxic or not, cause an impact to the environment, they are used as an indicator; the equivalent unit is the kilogram.

5.3. Sustainability and impact indicators

Some environmental indicators may be indifferently classified in the sustainability or the impact category.

5.3.1. Energy consumption

For computing this indicator it is necessary to determine the total energy consumption (renewable and non-renewable) of a process or activity. As, in general, processes evaluated consume a considerable quantity energy, the reference unit for this indicator is the megajoule (MJ).

5.3.2. Water consumption

This indicator, measured in kg of consumed water, quantifies the water required for producing a functional unit of a product, process or activity.

5.3.3. Oil consumption

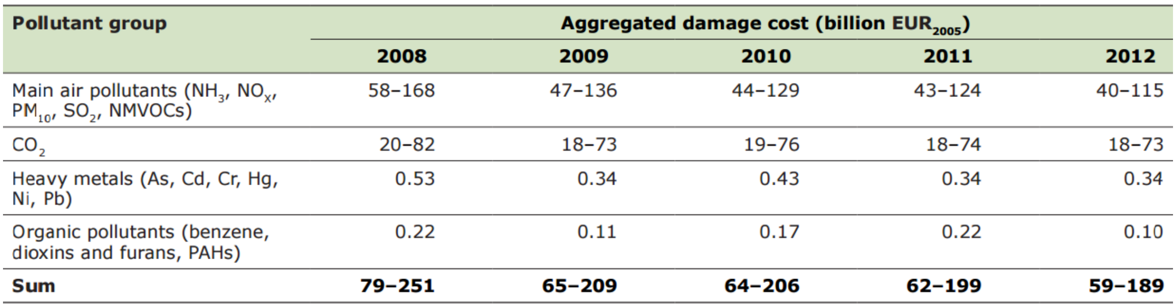
The indicator represents the oil consumption associated to a productive process. The reference unit is the kg.

5.4. Economic environmental indicators

Surprisingly, the environmental impact can also be assessed in terms of economic costs. Many methods and technical studies have been done in order to evaluate the damage caused to the environment in this way. The European Environment Agency (EEA) emits periodical reports in the matter based upon certain specific contaminating agents:

- Main air pollutants: ammonia (NH_3), nitrogen oxides (NO_X), particulate matter (PM_{10}), sulfur dioxide (SO_2) and non-methane volatile organic compounds (NMVOCs).
- Heavy metals: arsenic, cadmium, chromium, lead, mercury and nickel.
- Organic compounds: benzene, dioxins and furans, and polyclinic aromatic hydrocarbons (PAHs).
- Carbon dioxide (CO_2) [23].

A range of cost can be associated to each of these pollutants, as shown in Figure 5-3 – a table provided by the EEA in a 2014 study that showed the evolution of these indicators.



Pollutant group	**Aggregated damage cost (billion EUR$_{2005}$)**				
	2008	**2009**	**2010**	**2011**	**2012**
Main air pollutants (NH_3, NO_X, PM_{10}, SO_2, NMVOCs)	58–168	47–136	44–129	43–124	40–115
CO_2	20–82	18–73	19–76	18–74	18–73
Heavy metals (As, Cd, Cr, Hg, Ni, Pb)	0.53	0.34	0.43	0.34	0.34
Organic pollutants (benzene, dioxins and furans, PAHs)	0.22	0.11	0.17	0.22	0.10
Sum	**79–251**	**65–209**	**64–206**	**62–199**	**59–189**

Figure 5-3: Estimated damage costs aggregated by pollutant group, in billions of euros [23]

As it can be seen in the mentioned table, range of damage cost is vastly wide, due to the use of different methods and approaches in the calculations [23]. Damage costs decrease between those four years – apparently for the ongoing impacts of the environmental legislation and the lower rates of production in Europe due to the economic recession. However, the EEA states air quality still needs to improve in order to reduce harm to human health and the environment [23].

5.5. Use of environmental indicators

In this subsection, different environmental indicators are chosen to assess the environmental impact and sustainability of the considered process. Bearing in mind the possible experimental measurements (energy and water consumption, material inputs and outputs, generation of wastes, etc.) and which could be trustworthy indicators in the processes, selected indicators are the ones specified in table 5-1:

Category	*Indicator*
Sustainability	Biobased Feedstock*
	Global Warming Potential
Environmental Impact	Eco-indicator ‘99
	Wastes associated to production
Environmental impact and sustainability	Energy consumption
	Water consumption

Table 5-1: Selected environmental indicators

Biobased Feedstock (BF) – which is measured in kg – is an especially made-up indicator for this LCA. As all blends could be recycled, this indicator would not offer any differentiation. Instead, BF considers how many quantity of the raw material comes from renewable resources. Consequently, in the case of polymers, higher Biobased Feedstock will show less dependency on fossil fuels – which is an indicative of better sustainability. In this way, this new indicator will help in categorising the sustainability of the process far better than material subject to recycling.

6. Life Cycle Assessment (LCA)

Every product has its own life cycle, and each activity of the life cycle turns into an environmental impact due to resources consumption (e.g. raw material, energy and water); emission of substances to the landscape such as CO_2, radioactive waste, chemicals and particles; and other unnatural exchanges. This phenomenon is schematized in figure 6-1.

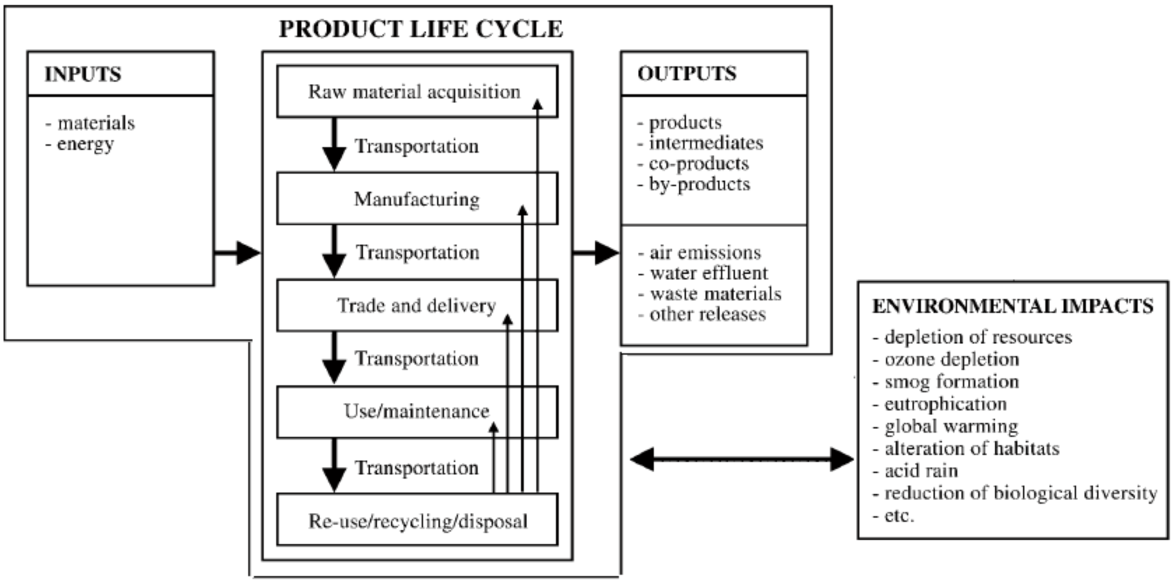


Figure 6-1: General Product Life Cycle structure and associated environmental impacts; adapted from [24]

Life Cycle Assessment (LCA) is an environmental management tool that enables to quantify the global impact of a particular product, process, service or group of activities [24]. In the specific case of polymer production and processing, most common stages can be included in the following categories: extraction of raw material, processing steps and waste management. LCA is a useful tool for reviewing both private and public business decisions, widely used in the improvement of goods and services. Hence, applications for this tool may be strategical planning, environmentally friendly development, product or process optimization, innovation and ecological improvements, among many others.

According to the scope of the LCA, there are four different types of analysis in the product manufacturing field: cradle-to-grave, cradle-to-gate, cradle-to-cradle or closed loop production, and gate-to-gate. Cradle-to-gate is the full LCA from resource extraction (cradle) to disposal phase (grave). Cradle-to-gate is an industrial commonly used assessment of partial product life cycle from product extraction (cradle) to the factory gate (i.e. before it is transported to the consumer).

Cradle-to-cradle is a specific LCA where the end-of-life disposal for the product is a recycling activity. Finally, gate-to-gate is a partial LCA looking at only one value-added process in the entire production chain, e.g. processing of a by-product to obtain another by-product. A complete cradle-to-gate evaluation might be formed by engaging cradle-to-gate with gate-to-gate modules as specified in their appropriate production chain.

The current study considers a particular gate-to-gate LCA of PLA processing and summarizes various cradle-to-gate assessments, which may be incorporated to the first one to generate a wider cradle-to-gate LCA.

6.1. Structure

LCA professionals quantify greenhouse emissions, resources consumption and other relevant environmental exchanges in every significant phase of the considered process. After data compilation, tabulation and a preliminary analysis of all the exchanges with the environment, it is compulsory a proper interpretation through the corresponding environmental indicators.

According to the ISO 14040 standards, there are distinguished four main phases in a LCA: Goal and Scope Definition, Inventory Analysis, Impact Assessment and Interpretation [24].

It is important to highlight that these phases are often interdependent – which means the result of one phase will influence on how the other phases are developed. Figure 6-2 shows the Life Cycle Assessment framework interactions.

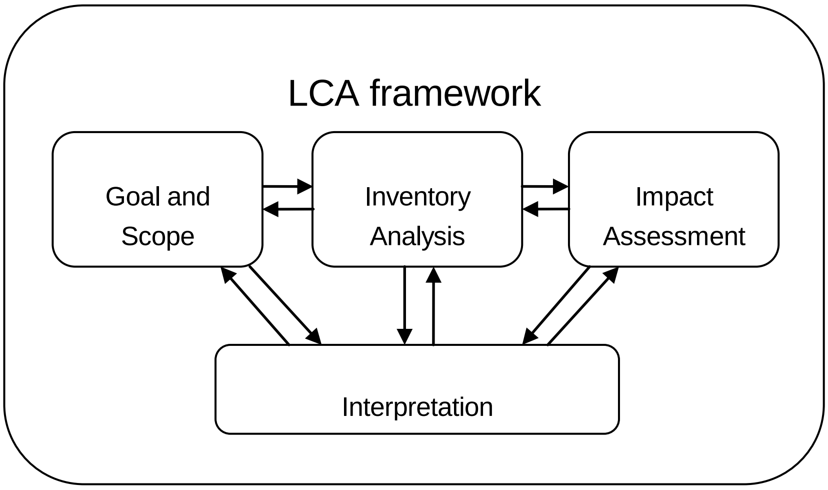


Figure 6-2: LCA phases interdependencies; adapted from [24]

6.2. Goal and scope

This stage sets out the context of the study and explains how and to whom the results are to be communicated. Therefore, it is a key step for understanding the purpose of the whole study; objectives must be clear and consistent with the intended application. In this phase, are defined the functional unit, the system boundaries, any assumptions and limitations and the allocation methods.

The functional unit is required to obtain a proper interpretation of the system and enables alternative goods, or services, to be compared and analyzed. It quantifies the service delivered by the product system, providing a reference to which the inputs or outputs can be related. In the case of study, the functional unit will be a kg of usable polymer blend. It is the easiest and one of the most accurate ways to take into account what is the environmental impact of the plastics processing.

System boundaries, assumptions and limitations will be defined in section 8.2.1, after all the materials, machines and methods have been explained or mentioned.

Finally, allocation methods are used when several products of functions share the same process, in order to partition the environmental load of the specific process. Most commonly allocation methods involve expansion, substitution or partition of the system, which is not always an easy proceeding, and may lead to different results depending on the methodology used [24]. As it is not the case for this study, it will not be further discussed.

6.3. Inventory Analysis

Inventory analysis, also called Life Cycle Inventory (LCI), involves creating inventory of flows for the product system, regarding the inputs and outputs of water, energy, raw materials, and releases to air, land and water. The flow is usually modelled with a flow chart that includes assessed activities and gives a clear picture of the technical system boundaries. It is important to highlight data must be related to the functional unit defined in the previous phase (goal and scope definition). At industry level, data level may be obtained by questionnaires fulfilled by operators. However, if this option is not possible or reliable, databases or data sets also might be used from previous studies. Care must be taken to ensure that the secondary data source reflects properly the studied system conditions.

6.4. Impact Assessment

Impact assessment is aimed at evaluating the significance of potential environmental impacts based on the inventory analysis flow results. In most cases, this LCA phase includes: selection of impact categories, category indicators and characterization models (for example, global warming); classification and assignation to specific impact categories of the inventory parameters (e.g. classification of CO_2 emissions inside global warming); and impact measurement into common equivalence units that are aggregated to provide an overall impact category total (e.g. modelling CO_2 potential impact on global warming).

Although most LCA finish at the characterization stage, normalization, grouping and weighting may be used in addition to the other impact assessment elements. Normalization consists of expressing environmental impact in a comparable way; grouping is sorting and possibly ranking the impact categories; and weighting allows adding up different environmental impacts categories to a single number for the total environmental impact. This last step is unadvised by the ISO 14044:2006, because it may reflect a high degree of subjectivity as a result of weighting [24].

6.5. Interpretation

Life cycle assessment interpretation is a systematic technique for identifying, quantifying, checking, and evaluating information provided by the inventory analysis and the impact assessment. The outcome of the interpretation phase is a set of conclusions and recommendations for the study, and should include:

- Identification of significant issues based on the results of the inventory analysis and impact assessment phases.

- Evaluation of the study considering completeness, sensitivity and consistency checks.

- Conclusions, limitations, recommendations [24].

Furthermore, in this stage, accuracy, completeness and consistency of the study are evaluated within the sensitivity of the data elements for a clear understating of the development of the LCA.

6.6. Eco-profiles of base materials

In this section, relevant data of previous documented Life Cycle Assessment of the polymers used in the pilot plant experiments will be exposed.

6.6.1. Eco-Profile of PLA

Polylactide acid used in the experiments is provided by Ingeo®, as the current LCA. The following table summarises the values of the environmental indicators chosen in section 5.5. All data is given for 1 kg of PLA at the factory gate (in pellet mode).

Category	*Indicator*	*Value*	*Units*
Sustainability	Biobased Feedstock (BF)	1	kg
	Global Warming Potential (GWP)	1.24	kg of CO_2 eq.
Environmental Impact	Eco-indicator ‘99	220	mPt
	Wastes associated to production	0.068	kg
Environmental Impact and sustainability	Energy consumption[1]	42.50	MJ
	Water consumption	48.79	kg

Table 6-1: Environmental indicators of the PLA Life Cycle Assessment; adapted from [25]

6.6.2. Eco-Profile of ABS

The LCA of ABS is provided by *PlasticsEurope*. In the below table (6-2) are summarized the selected environmental indicators for ABS.

Category	*Indicator*	*Value*	*Units*
Sustainability	Biobased Feedstock (BF)	0	kg
	Global Warming Potential (GWP)	3.10	kg of CO_2 eq.
Environmental Impact	Eco-indicator ‘99	400	mPt
	Wastes associated to production	0.018	kg
Environmental Impact and sustainability	Energy consumption	52.18	MJ
	Water consumption	150	kg

Table 6-2: Environmental indicators of the ABS Life Cycle Assessment; adapted from [26]

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[1] Energy consumption is referring – and from now on will always refer – to energy consumed in the process. It does not contemplate feedstock energy of the polymer.

6.6.3. Eco-Profiles of PA 610 and PA 1010

In the following tables (6-3 and 6-4) are shown the values for the selected environmental indicators, obtained from the eco-profiles provided by *PlasticsEurope*, of both types of polyamides used in the experiments.

Category	*Indicator*	*Value*	*Units*
Sustainability	Biobased Feedstock (BF)	0.62	kg
	Global Warming Potential (GWP)	4.6	kg of CO_2 eq.
Environmental Impact	Eco-indicator ‘99	660	mPt
	Wastes associated to production	0.140	kg
Environmental Impact and sustainability	Energy consumption	125.40	MJ
	Water consumption	185	kg

Table 6-3: Environmental indicators of the PA 610 Life Cycle Assessment; adapted from [27]

Category	*Indicator*	*Value*	*Units*
Sustainability	Biobased feedstock (BF)	1	kg
	Global Warming Potential (GWP)	4	kg of CO_2 eq.
Environmental Impact	Eco-indicator ‘99	640	mPt
	Wastes associated to production	0.171	kg
Environmental Impact and sustainability	Energy consumption	181.70	MJ
	Water consumption	160	kg

Table 6-4: Environmental indicators of the PA 1010 Life Cycle Assessment; adapted from [27]

7. Materials and methods

7.1. REX modification and compatibility of polymers

The term reactive extrusion (REX) refers to the intentional and controlled promotion of chemical reactions during continuous extrusion, as described in 4.2.5. This process is an attractive way of blending polymers with limited miscibility, thereby increasing the process window and versatility of the final product. In this framework, this study is centered on a blending of modified (REX) polylactic acid with other polymers:

- PA 610 (a partially bio-based polyamide)
- PA 1010 (a totally bio-based polyamide)
- ABS (an amorphous thermoplastic polymer)

7.2. Materials

In this subsection, the different feedstocks used along the project are specified: PLA, PAs, ABS, a compatibilizing agent and a chain extrusion agent. Nevertheless, as structure, synthesis, properties and applications of the mentioned bioplastics are specified throughout section 4, this subsection will only stipulate the commercial details of the products used.

7.2.1. PLA

The base material is the commercial product Biopolymer 4032D from Ingeo™ – see Annex A.1 – manufactured by NatureWorks®, headquartered in Minnetonka, Minnesota, USA. Based upon previous research in the CCP, this type of PLA has proved to show a greater structural modification to reactive extrusion. Henceforth, all references to PLA will be to this grade of PLA, since it is the only one used in the project.

7.2.2. Chain extending agent: SAmfE

SAmfE stands for Styrene-Acrylic multifunctional-Epoxide. It is an oligomeric compatibilizer agent that has previously proved to be a fine chain extender for PLA [9]. Figure 7-1 shows the generic structure of SAmfE, where R1-R5 are H, CH_3, a higher alkyl group, or a combination of them; R6 is an alkyl group and A, B and C are each between 1 and 20 [9].

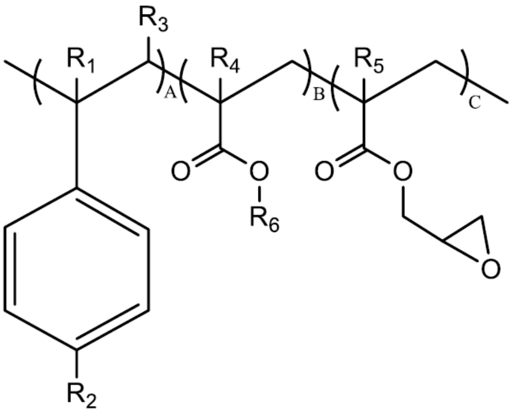

Figure 7-1: Structure of SAmfE (chain extending agent)

Specifically, ADR-4300 F Joncryl® commercial product marketed by BASF™ has been used for the experiments in the project. The Joncryl® ADR-4300 has high level of epoxy functionality, and is designed to act as a coupling agent to react with degraded polymers, for recovering their molecular weight and viscosity. Furthermore, it improves the recyclability of the polymer.

As Joncryl® F ADR-4300 will be the only grade used, it is possible to leave out the specific product code (ADR-4300 F) aside, and from now on use the codename Joncryl to refer to this commercial grade. In the product datasheet attached in Annex A.2 its features are specified.

7.2.3. PA 610 and PA 1010

Commercial grades Vestamid® *Terra* HS and Vestamid® *Terra* DS (see Annex A.3 and A.4) from Evonik Industries AG were the polyamides used in this project. The HS grade corresponds to a PA 610, with 62 % of material based on renewable resources, as it is the polycondensation of 1,6-hexamethylene diamine (H) and 1,10-decanedioc acid (sebacic acid – S) and the last monomer is extracted from castor oil. The DS grade is a PA 1010, based 100 % on natural resources, because both monomers that take part in polycondensation (1,10-decamethylene diamine and sebacic acid – S) are extracted from castor oil.

7.2.4. ABS

ABS Terluran® GP-22, which specifications are detailed in Annex A.5, is the ABS grade chosen for the project. It is manufactured by Styrolution™ and is a general purpose grade with good formability, high impact resistance and thermal distortion. For simplifications, as in the case of the PLA, the degree Terluran GP-22 will be called henceforth ABS, without specifically referring to its grade, since it is the only grade used in the project.

7.2.5. ABS-g-MAH

As mentioned in section 4.2.6, commercial grade of ABS-g-MAH has been selected to reconcile the ABS phase with the modified PLA (REX-PLA).

The Acrylonitrile Butadiene Styrene Maleic Anhydride grafted acid (ABS-g-MAH), is a modified ABS by adding a specific degree of maleic anhydride – which is an organic compound with the formula $C_2H_2(CO)_2O$. The high reactivity of the double bonds and the two carbonyl groups makes it suitable for the production of many substances. In the field of polymers, it is used as thermoplastic compatibilizer both for polyolefins as for styrenic polymers in presence of butadiene.

For the PLA-ABS blending, the commercial grade supplied by PolyramTM Bondyram® 6000 has been selected as compatibilizer. It is marketed in the pellets form, with a percentage of maleic anhydride between 0.6 % and 1 %. The attached datasheet in Annex A.6 shows its main characteristics. From now on, ABS-g-MAH will refer specifically to Bondyram® 6000 commercial grade.

7.3. Facilities

The R&D centre where the project was developed (*Centre Català del Plàstic)* has a wide range of facilities to research on different projects in the scope of plastic transformation and characterization. The main machines used in the course of the project are summarized on table 7-1:

Machine	Brand and model	Voltage (V)	Intensity (A)	Power (kW)
Dryer	*PIOVAN DSN506HE*	400		8.80
Dryer	*PIOVAN CH180*	400		9.00
Cooling circuit	*NOVAIR MTA TAE 051*	400	13.7	7.90
Compressor	*Fini E.C. Bravo 94M 23050*		14.6	2.20
Vacuum machine	*Asynchronous motor 80/80 IEC-34*			0.55
Twin-screw extruder	*CollinKneter 25X24D*	3x400/230	3x25	15.00
Annealing oven	*MLF*			4.0
Pelletizer	*IQAP GLI - I*	220		0.75

Table 7-1: Electrical specifications obtained from the technical sheets of the equipment used.

Besides, other minor equipment was used: a 20 dm^3 cooling bath, a volumetric feeder, and lighting.

7.4. Transformation processes

In this section the transformation processes that are needed for creating the blends will be covered. Basically, the purpose of these steps is enhancing the PLA properties by altering its structure and composition. On one hand, in the reactive extrusion of PLA to form REX-PLA, as a consequence of PLA degradation mechanisms and the action of the extruding agent molecular weight of the polymer is increased. Furthermore, sensibility in front of degradation mechanisms and temperature are decreased. On the other hand, when REX-PLA and another polymer (in our case, ABS or a polyamide) are blended in the extruder, the service temperature and life span of PLA are enlarged. Figure 7-2 shows principal steps of the described procedures.

Main materials are in yellow containers, while additives and processes are in orange and blue boxes, respectively. Letters A and B and discontinuous arrows represents the two possible blending paths – the compatibilizer ABS-g-MAH is only used with ABS.

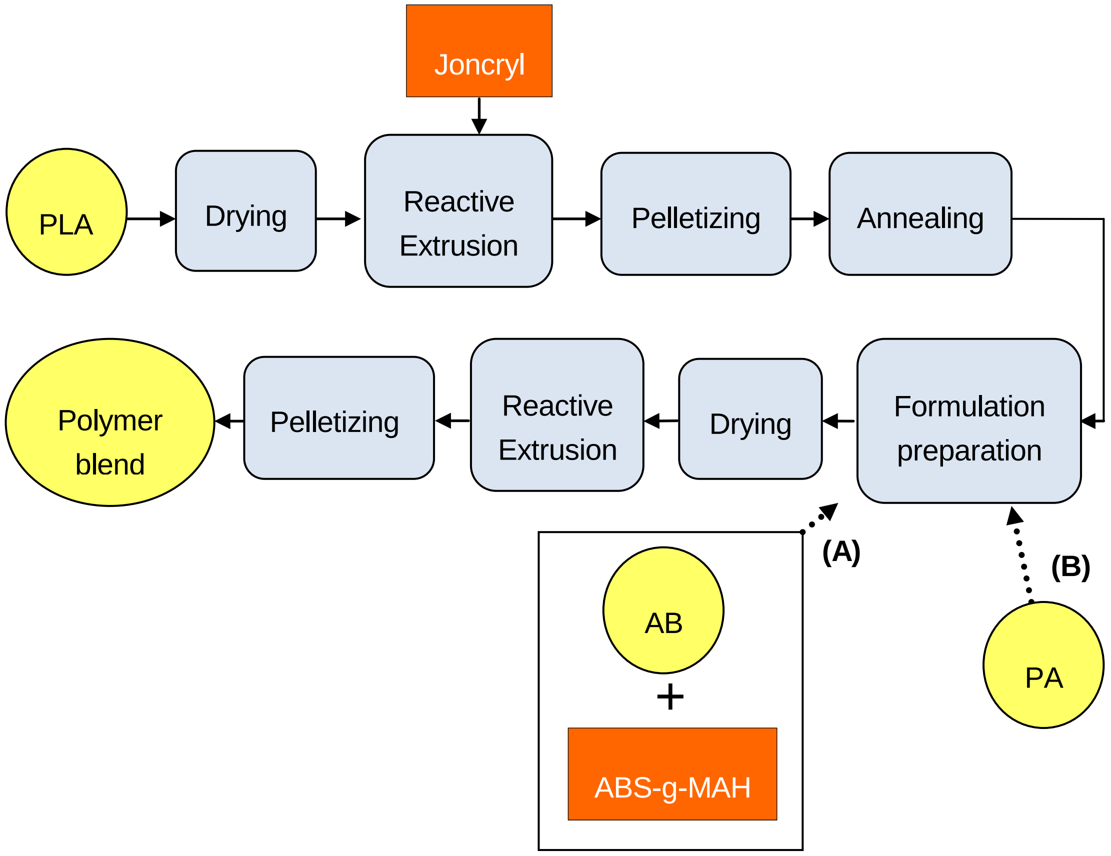

Figure 7-2: Main steps of the polymer blending

Although drying, pelletizing and annealing are simple operations that require only one or two pieces of equipment, reactive extrusion is a bit more complex (see figure 7-3). For this process, it is required calibration of the rationing systems, a cooling system for the extruded material, vacuum conditions and a nitrogen atmosphere to keep an adequate pressure.

In first place, calibration of the rationing systems is done by trying different engine speeds and precisely measuring the released mass by the volumetric feeder. This technique allows knowing the approximate mass flux in relation with the pre-set engine speeds, and after we can select the appropriate one according to the pursued purposes. In second place, the cooling takes place in a water cooling bath of 20 dm^3. Finally, a continuous flux of technical nitrogen is supplied for providing an atmosphere of 250 kPa.

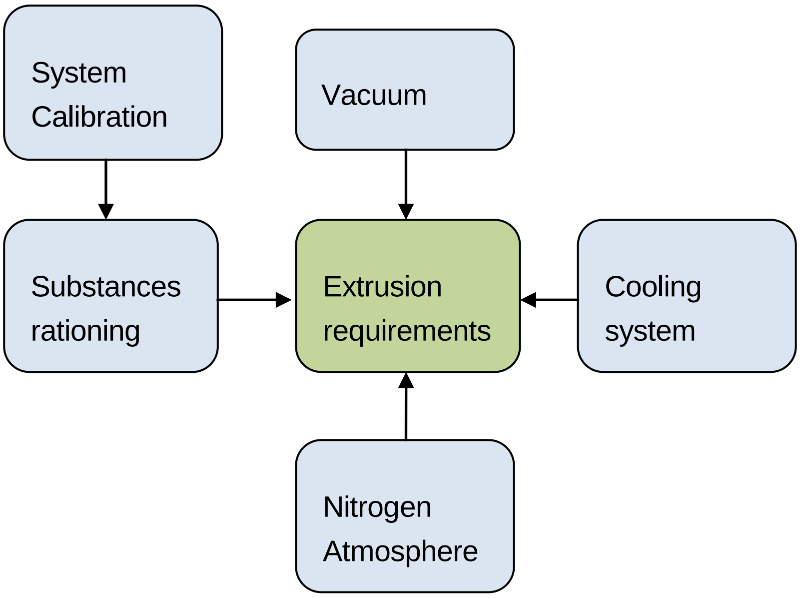

Figure 7-3: Extrusion requirements

7.4.1. Reactive extrusion REX-PLA preparation

In the first transformation phase, PLA structure and properties are altered by reactive extrusion. In the below tables 7-2 and 7-3 are detailed the equipment and materials used in this stage.

Equipment	Model
Twin-screw extruder	*CollinKneter 25X24D*
Dryer 1	*PIOVAN DSN506HE*
Dryer 2	*PIOVAN CH180*
Cooling circuit	*NOVAIR MTA TAE 051*
Pelletizer	*IQAP GLI - I*
Compressor	*Fini E.C. Bravo 94M 23050*
Vacuum machine	*Asynchronous motor 80/80 IEC-34*
Volumetric feeder	*Lap Policolor*

Table 7-2: Equipment used in REX-PLA production

Material	Commercial grade	Codename
PLLA	Ingeo™	*PLA*
styrene-acrylic multifunctional-epoxide agent	Joncryl® ADR-4300	*Joncryl*

Table 7-3: Materials and respective codenames used in REX-PLA production

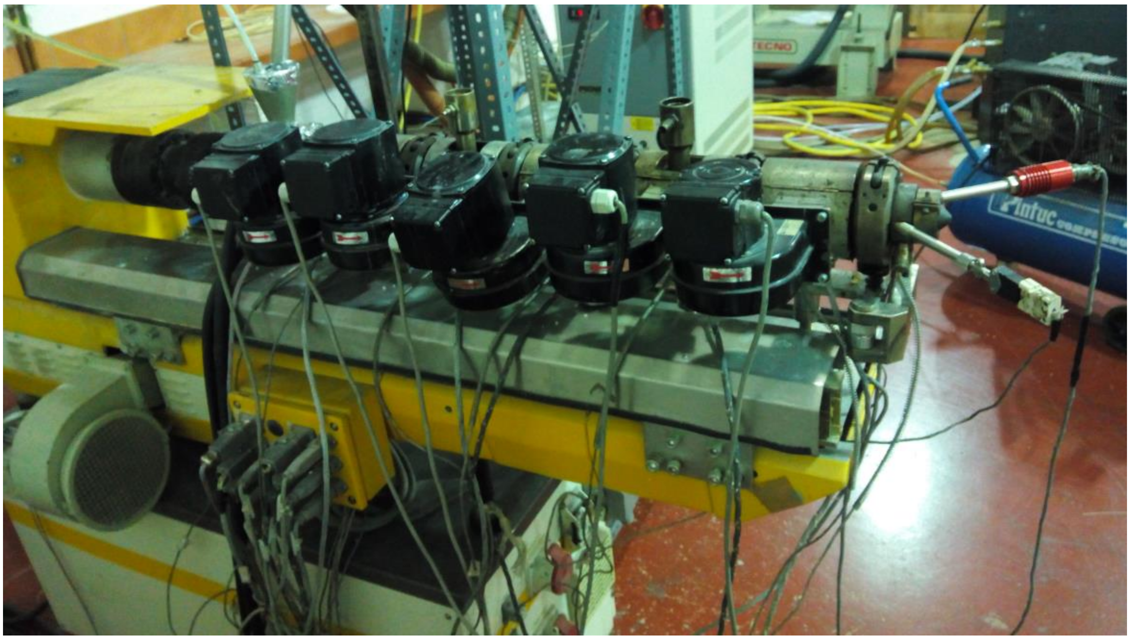

Figure 7-4: Picture of the twin-screwed extruder from the CCP

The above image (figure 7-4) shows the extruder from the pilot plant. It has seven different heat zones, in order to apply a specific temperature profile. The profile applied is the specified in table 7-4 – where heat zone one is near to the alimentation and heat zone 7, near to the extruder's die. The engines of the feeders are set to distribute the chain extending agent to obtain a REX-PLA with 1.5 % in mass of Joncryl. Within two days of production, 12 kg of REX-PLA were produced.

	Heat Zone	1	2	3	4	5	6	7
Temperature (ºC)	**Day 1**	150	170	180	190	195	200	200
	Day 2	165	195	205	215	225	230	220

Table 7-4: Temperature profile applied in reactive extrusion of REX-PLA

The proceeding of REX-PLA production is described as follows: PLA is dried at 80 ºC for four hours in a hopper with an air compressor drying system. Afterwards, the cooling system and the extruder are turned on and the above temperature profile for the latter one is applied. The vacuum system is activated and the stopcock of nitrogen administration is opened, to provide a pressure of 250 kPa. Both feeders (PLA and Joncryl) are adjusted to the proper speed and the extruder is triggered. Once the extruded material has been enough time (approximately the residence time) in the cooling bath, REX-PLA must be stored. All along this process, the rotational speed, the extruder die pressure and the instant intensity consumed by the machine is monitored, to ensure in real time that there are not anomalies in the process.

The amorphous phase of PLA starts to flow at temperatures superior to the glass transition temperature (Tg), which is approximately 60 ºC. As PLA needs being dried (for four hours at 80ºC) before any conformation procedure, recrystallization is indispensable. Therefore, once REX-PLA is obtained, it is necessary to apply to the pellets an annealing technique, in order to maximize the crystallinity of the material. For that purpose, a stove with forced air circulation is used.

7.4.2. Polymer blends preparation

When preparation of PLA is accomplished, next step is preparing the blending with the other polymers. Three different blends were made:

- REX-PLA with ABS and the compatibilizer ABS-g-MAH
- REX-PLA with PA 610
- REX-PLA with PA 1010

Independently of the studied blend – except for the materials – methods and conditions are almost the same. A preliminary step done in the pilot plant was to prepare the blends in a small scape, using a measuring mixer (Brabender Plastic Corder W50EHT). However, as this phase is only required once to characterize the blends, it will not be explained nor considered in the Life Cycle Assessment.

The equipment used to prepare the polymer blends is the same shown in table 7-2. The thermal history selected for the blends is the same that was applied to REX-PLA.

The proceeding starts off preparing every formulation in the desired proportions. In our case will be the ones specified in table 7-5. After, every blend is dried for 4 hours at 80 ºC. The next step is the reactive extrusion, in which vacuum and the nitrogen atmosphere of 250 kPa are applied. Extruded material is then annealed and stored for further characterizations that do not contemplate this project. A total of 9.8 kg of blends were obtained, between 3 and 4 kg of each blend type. Similarly to the REX-PLA extrusion, rotational speed, die pressure and machine intensity were monitored.

Formulation	Codename
70% REX-PLA, 24% ABS, 6% ABS-g-MAH	REX-PLA/ABS
80% REX-PLA, 20 % PA 610	REX-PLA/PA 610
80% REX-PLA, 20 % PA 1010	REX-PLA/PA 1010

Table 7-5: Formulations prepared for the reactive extrusion

8. Results and discussion

In this section, results of the experiments will be exposed and discussed – in particular, those with relation with the sustainability and environmental impact of the transformation processes.

8.1. Data summary

In all the experiments, the conditions specified in table 8-1 were applied in the reactive extrusion process. Table 8-2 describes material inputs and outputs, as well as extruding time – as 4 hours of drying and 4 hours of annealing were fixed in all production days.

Feeder Speed (rpm)	850
Cutter's Speed (m/s)	540
Screw Speed (rpm)	100

Table 8-1: Parameters used in the reactive extrusion

Formulation	*Total Input: m_i (kg)*	*Blend Output: m_b (kg)*	*Extruding time (minutes)*
REX-PLA	7*	5.3	154
REX-PLA	7	6.7	88
REX-PLA/ABS	4	3.5	55
REX-PLA/PA 610	4	3.2	52
REX-PLA/PA 1010	4	3.1	48

Table 8-2: Inputs, outputs and extruding time of the different formulations created

As it can be seen in table 8-2, some material is wasted as result of the process. The input of the first REX-PLA row is marked with an asterisk because it was the first production day and 1.5 kg were used in order to purge and calibrate the extruder.

8.2. Gate-to-gate LCA

This section is dedicated to define, quantify, analyse and compare the Life Cycle Assessment of the transformation processes described in section 7.4.

8.2.1. Goal and Scope

The scope of this *gate-to-gate* analysis includes two main transformation processes. The first one is REX-PLA production, by reactive extrusion of PLA and a chain extending agent. The second transformation process contemplates blending of the obtained REX-PLA with other polymers, also with reactive extrusion techniques. In particular, there are three different possibilities of blends studied: REX-PLA/ABS, REX-PLA/PA 610 and REX-PLA/PA 1010. The functional unit, as mentioned before, will be the kg of usable polymer blend.

8.2.2. Life Cycle Inventory

In this subsection, process described in figure 8-2 will be breakdown in three different stages, to identify the raw materials, energy and water flows of inputs and outputs in each phase.

8.2.2.1. Drying

Drying is the preliminary step applied to PLA – or each formulation that contains it – before beginning the reactive extrusion, in order to reduce its degradation mechanisms. Different formulations are obtained by physically blending the polymers pellets. To each formulation, 4 h of drying to 80 ºC are applied. The machines used in this procedure are PIOVAN DSN506HE or PIOVAN CH180 and air compressor Fini E.C. Bravo 94M 23050. Figure 8-1 shows a diagram illustrating inputs and outputs of this procedure.

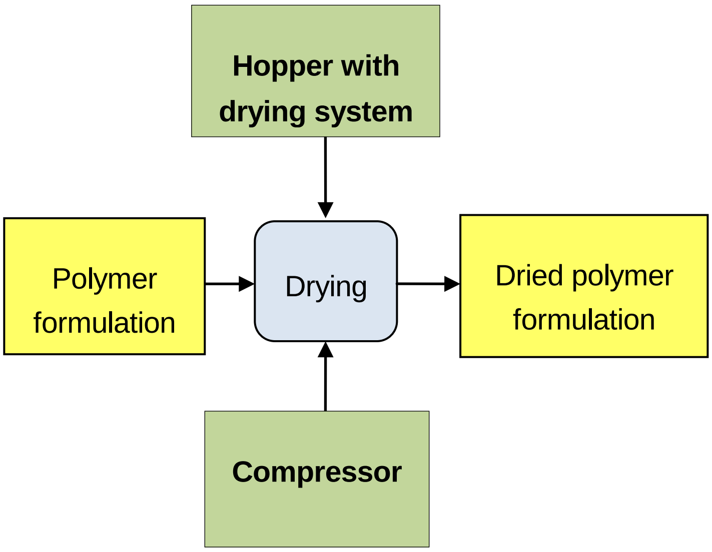

Figure 8-1: Flow diagram of the drying stage

8.2.2.2. Extruding

As explained in previous sections, reactive extrusion has the following specific requirements: substances rationing, N_2 atmosphere, vacuum conditions and a cooling system. Figure 8-2 shows the inputs and outputs of this process; as calibration and purge is only needed the first day of extrusion, it is not shown in the reactive extrusion flow, but will be taken into account in the impact assessments calculations. Joncryl is only added when the formulation is pure PLA.

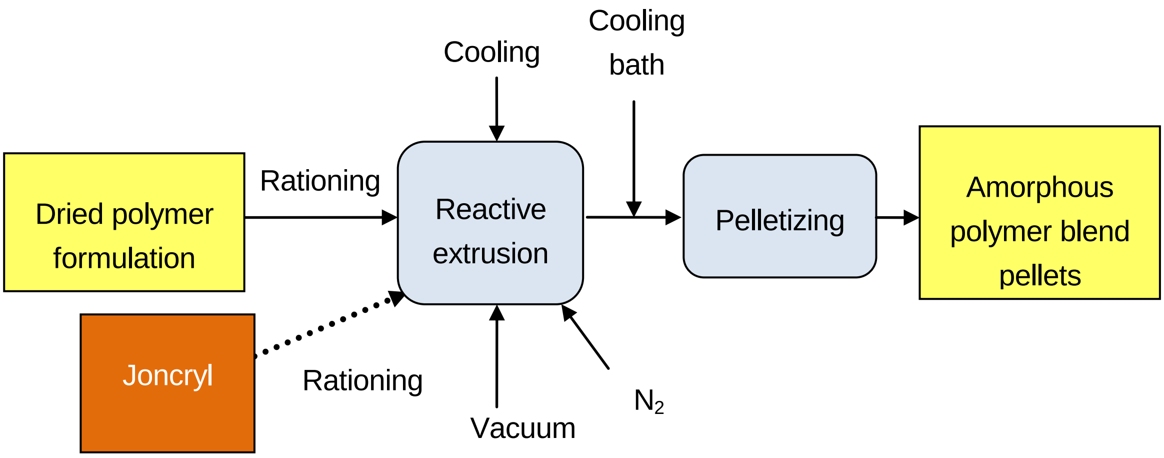

Figure 8-2: Flow diagram of the reactive extrusion stage

8.2.2.3. Annealing

Once obtained the pellets, it is required to submit the polymer blend to an annealing process. The pellets are placed in aluminium trays, and these, in an oven with forced air circulation. Figure 8-3 is a picture of the annealing oven used in the pilot plant.

Figure 8-3: Picture of the annealing oven of the CCP

8.2.3. Inventory Analysis

Indicators, impact categories, and characterization models are chosen aligned specified in subsection 5.5 and used in 6.6. This way, it will be possible to compound a cradle-to-gate analysis by adding the eco-profiles of the base materials to the current LCA.

Inside the category of sustainability, Biobased Feedstock and Global Warming Potential (GWP) will be measured in kg and kg of CO_2 equivalent, respectively; the indicators chosen for environmental impact are the Eco-indicator '99 (measured in mPt) and wastes associated to production (measured in kg); finally, energy consumption (MJ) and water consumption (kg) will be used as both environmental impact and sustainability indicators. All these indicators are given per functional unit (kg of polymer blend).

8.2.4. Impact Assessment

In this section, calculations of these indicators will be justified, and summarised in table 8.3 (subsection 8.2.4.7).

8.2.4.1. Biobased Feedstock (BF)

As biodegradable feedstock of each base material was specified in sections 6.6, it is fairly easy to determine the Biobased feedstock in each blend formulation (BF_b), as from the biodegradability of the different polymers (BF_i) and the formulations proportions of the polymer blends ($x_{b,i}$).

$$BF_b = \sum_i x_{b,i} \times BF_i \qquad \text{(Eq. 1)}$$

8.2.4.2. Wastes associated to production

Some material is lost in the transformation processes. This leads to wastes associated to production, which can be calculated by subtracting the mass output of each polymer blend (m_b) specified in in table 8-2 from the input (m_i) provided in the same table, and then dividing this result by m_b.

$$Wastes_b = \frac{m_b - m_i}{m_b} \qquad \text{(Eq. 2)}$$

8.2.4.3. Water Consumption (WC)

Water is used to refrigerate for two different purposes. The first one involves cooling the extruder during the reactive extrusion, which is done with a closed cooling circuit, and therefore, there is no water waste. The second one is for cooling the polymer blend after it is extruded. For this matter, it is applied a constant flow of water in the 20 dm^3 cooling bath. The water consumption of each polymer (WC_b) was calculated as follows:

$$WC_b = \frac{V_{bath}}{t_{fill}} \times \frac{t_{eb}}{m_b} \qquad \text{(Eq. 3)}$$

Dividing the volume of the bath (V_{bath}) by the time necessary to completely fill it (t_{fill}), we obtain the water flow. Water consumed by kg of blend is calculated by multiplying the flow to the rate time of extrusion (t_{eb}) per mass of blend produced (m_b).

8.2.4.4. Energy Consumption

For the drying stage, energy consumed is computed by multiplying the power of the machines used – the air compressor and the drying system of the hopper – by the drying time and applying a correcting factor of 0.4, suitable for this type of processes [7]. The output then must be divided by the produced mass of each polymer blend.

$$E_{db} = \sum_{j} \frac{0.4 \times P_j \times t_d}{m_b} \qquad \text{(Eq. 4)}$$

Where E_{db} is the energy consumed for each blend in the drying stage; P_j is the power of each machine used in the drying stage; t_d the time for drying; and m_b the mass of each polymer blend.

The energy consumed in the annealing stage is calculated in a similar way (taking into account the annealing time and the power consumed by the annealing oven).

$$E_{ab} = \frac{0.4 \times P_{oven} \times t_a}{m_b} \qquad \text{(Eq. 5)}$$

Where E_{ab} is the energy consumed for each blend in the annealing stage; P_{oven} is the power of the annealing oven; t_a the time for annealing; and m_b the mass of each polymer blend.

Lastly, for the extruding phase, the energy consumed is calculated as follows:

$$E_{eb} = \frac{t_{eb}}{m_b} \times \left(0.9 \times \frac{N_{act}}{N_{\max}} \times P_{extr} + \sum_{k} 0.4 \times P_k \right) \qquad \text{(Eq. 6)}$$

Where E_{eb} is the energy consumed for each blend in the extruding stage; t_{eb} and m_b are the time of extrusion and the mass of each polymer blend; N_{act} and N_{max} are the actual (100 rpm) and maximum (260 rpm) rotational speed of the extruder screw, respectively; P_{extr} is the power of the extruder and P_k is the power of the other machines used in the extruding stage. The energy consumed by the extruder is calculated as proposed by Rauwendaal et al [28].

The extra energy consumed by lighting is calculated as the accumulated power of the lab lights (a large, a small fluorescent and a mercury lamp) multiplied by the total processing time of each polymer blend.

$$E_{xb} = (t_d + t_a + t_{eb}) \times \sum_l P_l \qquad \text{(Eq. 7)}$$

Summing up the energies required in the three stages for each polymer blend – and an extra term for lighting – we can obtain the energies required for the different blends.

$$E_b = E_{db} + E_{ab} + E_{eb} + E_{xb} \qquad \text{(Eq. 8)}$$

8.2.4.5. Global Warming Potential (GWP)

GWP of each polymer blend is calculated based on the energy consumed for their transformation, by applying the relation of Spain energetic mixture: 1 kWh = 0.264 kg of CO_2 equivalent.

$$GWP_b = E_b(kWh) \times \frac{0.264}{kWh}\ \text{kg of } CO_2 \qquad \text{(Eq. 9)}$$

8.2.4.6. Eco-indicator ’99 (EI’99)

Following the guidelines of the Environmental Impact ’99 manual for designers [16], the only sections assessable for our gate-to-gate LCA are production processes and waste processing and recycling. Materials are not contemplated because they will be covered on the 8.3 *cradle-to-gate* section; otherwise we would be adding up twice the environmental impact of the feedstock.

On one hand, low voltage (<1000 V) electricity used has an indicator of 27 mPt/kWh and water for processing has an indicator of 0.0026 mPt / kg [16]. On the other hand, ABS wastes have an indicator of 4.1 mPt/kg, and PA wastes of 2.5 mPt/kg [16]. PLA, being fully biodegradable, it is considered of not having any impact. Summing up, eco-indicator ’99 for each blend is calculated as follows:

$$EI'99_b = \sum_i Indicator_{i,b} \times Amount_{i,b} \qquad \text{(Eq. 10)}$$

8.2.4.7. Impact assessment results

Codename	*Formulation*	*Biobased Feedstock (kg)*	*Wastes associated to production (kg)*	*Water consumption (kg)*	*Energy consumption (MJ)*	*GWP (kg of CO_2 eq.)*	*EI ’99 (mPt)*
REX-PLA[1]	100% REX-PLA	1	0.045	39.05	23.32	1.71	175
REX-PLA/ABS	70% REX-PLA, 24% ABS, 6% ABS-g-MAH	0.7	0.143	46.79	38.97	2.86	294
REX-PLA/PA 610	80% REX-PLA, 20 % PA 610	0.924	0.252	48.39	35.54	2.61	269
REX-PLA/PA 1010	80% REX-PLA, 20 % PA 1010	1	0.290	45.94	36.06	2.64	273

Table 8-3: Selected indicators values for each polymer blend produced, as results of the application of the equations 1-10

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[1] For the REX-PLA formulation, it was considered the information available of the second day of extrusion, without taking into account purging.

8.2.5. Interpretation

Regarding the different results for indicators, the REX-PLA formulation is the friendlier blend to the environment, because it has a better score in all categories. However, we cannot compare this blend with the others because it has different purposes. While REX-PLA blend is meant to substitute PLA, the three other blends are intended to substitute the corresponding polymer (ABS or PA). All three have similar scores for water and energy consumption, as well as the eco-indicator '99 and the global warming potential. Contrarily, wastes associated to production were higher in the blends containing polyamides, because the transition stage was longer than in the REX-PLA/ABS blend – which leads into losing more material. Finally, blends with polyamides have more biobased feedstock for two reasons: they have a higher amount of PLA and the polyamides are partially or totally biobased. It seems the three blends are in a technical draw, so one or other would be chosen by the desired purpose.

8.3. From cradle-to-gate

Finally, we can add up to the different blends the eco-profiles of the different feedstock weighted by the formulation proportions to each polymer blend, in order to create a wider cradle-to-gate LCA. Results are summarised in table 8-4, together with the eco-profiles already provided in section 6.6.

Indicator / Blend	REX-PLA/ ABS	ABS	REX-PLA/ PA 610	PA 610	REX-PLA/ PA 1010	PA 1010
Biobased Feedstock (kg)	0.7	0	0.924	0.62	1	1
Wastes associated to production (kg)	0.196	0.018	0.334	0.140	0.379	0.171
Water consumption (kg)	92.19	150	124.42	185	116.97	160
Energy consumption (MJ)	84.37	52.18	94.62	125.40	106.4	181.70
GWP (kg of CO_2 eq.)	5.4	3.10	4.5	4.6	4.4	4
EI'99 (mPt)	568	400	577	660	577	640

Table 8-4: Comparison of the indicators with the feedstock polymers

This way, we are able to environmentally compare the original polymer with the theoretically equivalent blend with REX-PLA – it would be necessary to characterise each blend to make sure it would meet the requirements of the application required.

Starting off with ABS, we see only two indicators of the six chosen in which the blend with REX-PLA is environmentally better than the petro-based polymer alone: biobased feedstock and water consumption (almost a saving in 40% of water). Wastes associated to production may be higher because the experiments were done in a pilot plant. Once the process is stabilized and/or done in a larger scale, this indicator would surely decrease its value. Finally, energy consumption, global warming potential and the eco-indicator ’99 are higher – and therefore worse – in the case of the blend. After all, this blend seems not to be environmentally friendlier than ABS.

On the contrary, for both polyamides results are much more promising. In the case of PA 610, its blend with REX-PLA improves the sustainability and reduces the environmental form PA 610, according to all the indicators but one: wastes associated to production. Savings in water consumption exceed the 30 % and energy consumption is decreased in a quarter, and biobased feedstock is increased in almost a 50 %. GWP and EI’99 are also somewhat better in the blend than the assessed in PA 610 alone. Likewise, all indicators – except wastes associated to production and GWP – in the REX-PLA/PA 1010 blends suggest an improvement in the environmental performance over PA 1010. Energy savings are quantified in a 41 %, and water savings in a 27 %; while EI’99 is a 10 % lower, and GWP a 10% higher.

In conclusion, both polyamides blends with REX-PLA show an overall reduced environmental impact and improved sustainability. Furthermore, if the transformations were done on an industrial scale, the transition stage would be smaller compared to the stationary regime because extrusion time would be increase at the time drying and annealing would remain the same. Bearing in mind that this fact could easily decrease wastes associated to production, there is no doubt these blends would be much less harmless to the environment than the current used polyamide (PA 610 and PA 1010).

9. Economic Study

Direct and indirect costs of the present work involve human capital, processing expenditures, and mobility costs. The calculation for the various costs will be considered as if a company had hired the different services for the realization of the project, and the breakdown for these concepts are shown in the below tables 9-1 to 9-3.

Activity	*Quantity (h)*	*Unit price (€/h)*	*Cost (€)*
Research	120	15	1800
Experimentation	20	20	400
Memory redaction	150	15	2250
SUBTOTAL	**290**	**-**	**4450**

Table 9-1: Project costs associated to human capital

Cost related to use of equipment are stipulated in the current rates of the *Centre Català del Plàstic*.

Equipment	*Use (h)*	*Rates (€/h)*	*Cost (€)*
Collin Kneter 25X24D Twin-screw extruder	10	210	2100
PIOVAN DSN506HE Dryer	20	40	800
Annealing oven	20	50	1000
SUBTOTAL	**50**	**-**	**3900**

Table 9-2: Project costs associated to processing expenditures

Concept	*Quantity*	*Rates (€/h)*	*Cost (€)*
Train bonus ticket	1 ticket	37 €/ticket	37
Gasoline consumption	9.6 liters	1.04 €/liter	10
SUBTOTAL		**-**	**47**

Table 9-3: Project costs associated to mobility costs

All these disaggregated costs sum up **8397 €**, which is the total cost of the project.

10. Project Schedule

The following Gantt diagrams shows the approximate planning of the realization of this project.

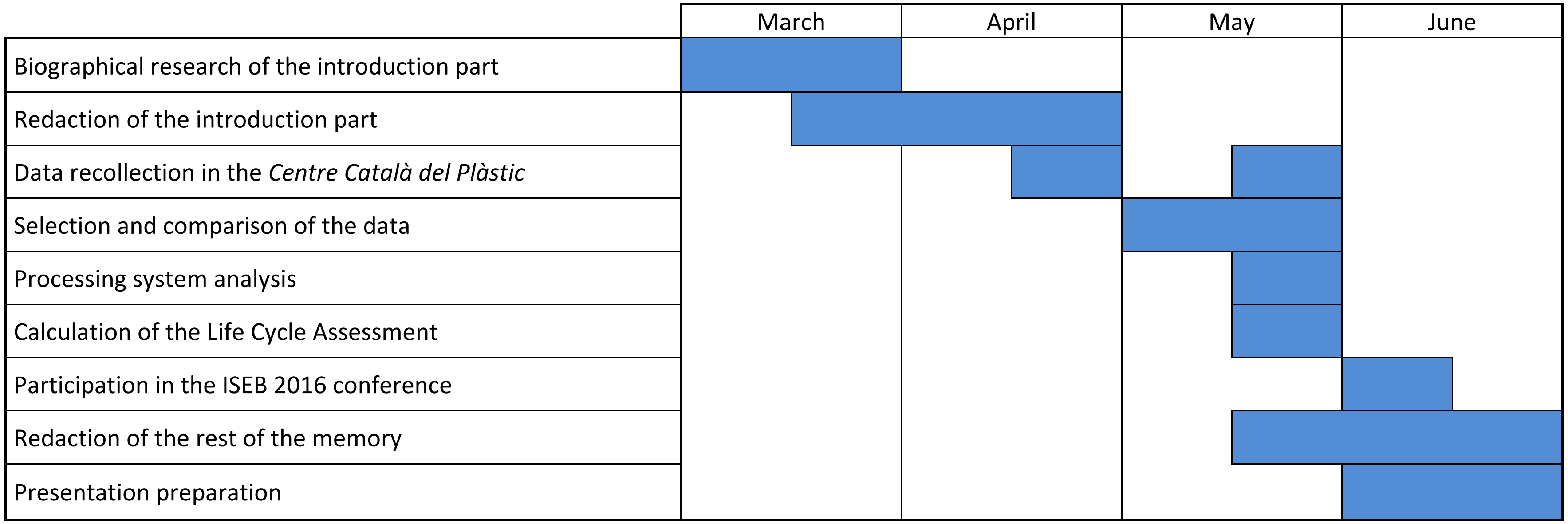

Figure 10-1: Gantt diagram of the project planning

11. Environmental Impact

Environmental impact of the project can be quantified by energy and water consumption. Energy consumption has three different origins: use of facilities in the pilot plant, means of transport, and the computer for writing the memory.

For the first item, consumed energy per kg of polymer blend was already calculated in section 8.2.4.4 as equations 4 to 8. Total consumed energy by the use of facilities will be the summation of the values – multiplied by every quantity produced – for the different blends. Means of transport used were the train and the car. Bearing in mind that a train has an average energy efficiency of 0.35 MJ / passenger km and a diesel car of 2.98 MJ/km, energy consumed by means of transport can be calculated by multiplying these values by the distance travelled by each vehicle (337.6 km by train and 84.4 km by car). Finally, energy consumed by the computer can be calculated knowing its power is of 160 W, and that it was used approximately for 270 hours. Therefore, total energy consumption can be calculated as follows:

$$E_{cons} = \sum_{b} (m_b \times E_b) + EE_{train} \times d_{train} + EE_{car} \times d_{car} + P_{PC} \times t_{PC} \times \frac{3.6 \times 10^{-3}\, MJ}{Wh} \qquad \text{(Eq. 11)}$$

Where E_{cons} is the project total energy consumed (MJ), m_b and E_b are the mass (kg) and the energy consumed of each blend (MJ/kg), EE_{train} and EE_{car} (MJ/km) are the average energy efficiency of trains and cars, d_{train} and d_{car} (km) are distances covered by train and by car; and P_{PC} (W) and t_{PC} (h) are the power and time of computer use. Following eq. 11, energy consumed in the course of the project is 1166.9 MJ (or 324.14 kWh), which has an equivalent impact of 85.6 kg of CO_2 (1 kWh = 0.264 kg of CO_2 equivalent).

Water consumption (WC in kg) corresponds to the use of the cooling bath. Knowing water consumption/kg (WC_b in kg of water/kg of blend) calculated for each blend in section 8.2.4.3 and output mass for the different blends (m_b in kg of blend) detailed in section 8.1, total water consumption can be calculated as follows:

$$WC = \sum_{b} m_b \times WC_b \qquad \text{(Eq. 12)}$$

According to eq. 12, total water consumption is of 722.6 kg.

12. Conclusions

This project meets its general pursued objective: assess the environmental impact and sustainability of blends of modified polylactic acid with other polymers (ABS and PA), through accomplishing its different specific objectives.

In first place, after exposing the vital importance of the sustainability of polymers due to its large use, and the immediate urgency to take action and reduce the environmental impact they create, it seems obvious to invest scientific resources on this matter. Bioplastics, which are biodegradable and/or biobased, are the focus of this research. In particular, introducing PLA properties and applications has given an idea of the potential of this biodegradable thermoplastic polyester. Furthermore, structurally modifying this polymer by reactive extrusion is a fine way to improve its degradation behaviour.

In second place, revealing the great quantity of environmental indicators, and categorizing them has helped choosing the ones selected for the studied gate-to-gate Life Cycle Assessment. They sometimes show disperse results for assessing the same activity, so it is crucial to use several indicators, focusing on the ones that have interest for evaluating the environmental impact and sustainability of the particular process or product studied.

Lastly, once the processes made in the pilot plant in Terrassa have been explained and LCA has been done and analysed, transformation processes applied seem quite satisfying, speaking from an environmental point of view. Adding up the eco-profiles of the different feedstock to the gate-to-gate Life Cycle Assessment made possible to environmentally compare the different blends with its equivalents – presumably, in this case, the polymers added to the different REX-PLA blends.

Although the REX-PLA and ABS reactive extrusion blend was found to be less sustainable than the ABS alone – reinforcing the need of LCA in the conception of new materials – blends produced by reactive extrusion of REX-PLA with polyamides PA 610 and PA 1010 have proven to be relevantly more environmentally friendlier than the respective polyamides themselves. Energy savings are quantified in 24.5 % and 41.4 %, and water savings would be of 32.7 % and 26.9 % when using the PA 610 and PA 1010 blends with REX-PLA, compared to the polyamide alone. Certainly, it is necessary to deeply characterize these blends to determine in which applications the current polyamide could be replaced by the REX-PLA blend.

In conclusion, REX-PLA blends with polyamides by reactive extrusion seem quite promising and should be the aim of further research, to help ensuring an adequate environment development.

13. Gratitude

I am very thankful to my tutor, Jordi Bou, for his reception, guidelines and help during the entire project. I similarly would like to thank Nil Constants and all the research staff of CCP for their warm receive and support.

Besides, I would like to thank the encouragement and patience of my parents, for supporting me on this journey and for bringing me a higher quality education. Last but not least, I would like to thank to Anna, for cheering me up when times were tough.

Scientific communication of the results of this work

The 10th International Society for Environmental Biotechnology (ISEB) conference was held in Barcelona on 1 to 3 of June 2016. In attendance, I had the honour of presenting an abstract of this project. I would like to expressly thank Jordi for this opportunity and new experience, which I really enjoyed, in the company of worldwide scientific experts.

The programme consisted on numerous 20-minutes conferences, more than a hundred poster presentations and 20 matchmaking sessions, all works ranging different applications and topics in the environmental and biotechnology sector. I partook in the modality of poster presentation (see Annex B). Furthermore, a special issue of the journals will be released compiling the best papers presented at ISEB 2016 in the scientific journal *Science of the Total Environment*– in which a summary of this work will be included.

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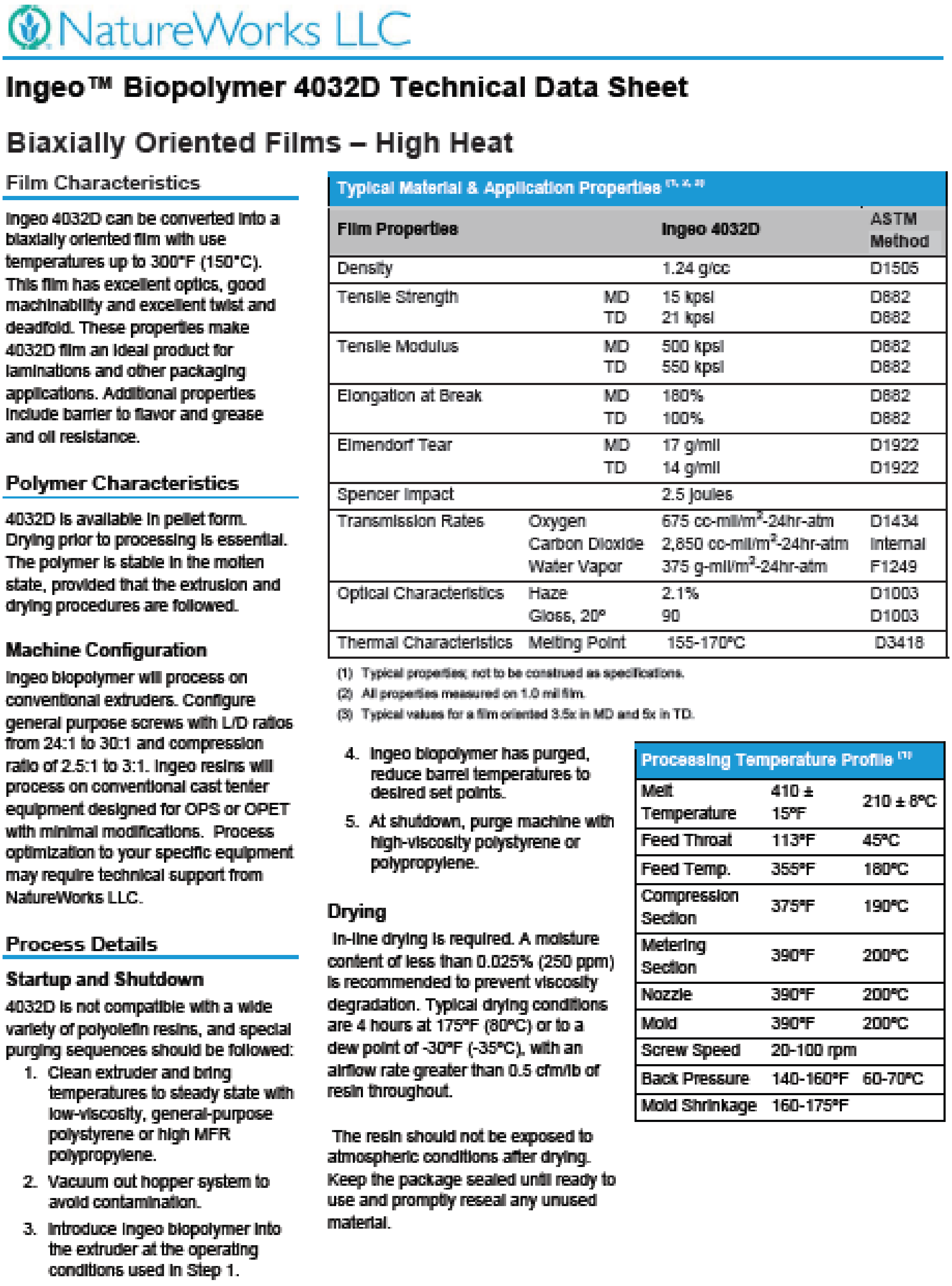
Annexes

Annex A: Material Datasheets

A.1. NatureWorks LLC Ingeo^{TM} Biopolymer 4032D (PLA)



NatureWorks LLC

Ingeo™ Biopolymer 4032D Technical Data Sheet

Biaxially Oriented Films – High Heat

Film Characteristics

Ingeo 4032D can be converted into a biaxially oriented film with use temperatures up to 300°F (150°C). This film has excellent optics, good machinability and excellent twist and deadfold. These properties make 4032D film an ideal product for laminations and other packaging applications. Additional properties include barrier to flavor and grease and oil resistance.

Polymer Characteristics

4032D is available in pellet form. Drying prior to processing is essential. The polymer is stable in the molten state, provided that the extrusion and drying procedures are followed.

Machine Configuration

Ingeo biopolymer will process on conventional extruders. Configure general purpose screws with L/D ratios from 24:1 to 30:1 and compression ratio of 2.5:1 to 3:1. Ingeo resins will process on conventional cast tenter equipment designed for OPS or OPET with minimal modifications. Process optimization to your specific equipment may require technical support from NatureWorks LLC.

Process Details

Startup and Shutdown

4032D is not compatible with a wide variety of polyolefin resins, and special purging sequences should be followed:

1. Clean extruder and bring temperatures to steady state with low-viscosity, general-purpose polystyrene or high MFR polypropylene.
2. Vacuum out hopper system to avoid contamination.
3. Introduce Ingeo biopolymer into the extruder at the operating conditions used in Step 1.
4. Ingeo biopolymer has purged, reduce barrel temperatures to desired set points.
5. At shutdown, purge machine with high-viscosity polystyrene or polypropylene.

Typical Material & Application Properties (1, 2, 3)

Film Properties		Ingeo 4032D	ASTM Method
Density		1.24 g/cc	D1505
Tensile Strength	MD TD	15 kpsi 21 kpsi	D882 D882
Tensile Modulus	MD TD	500 kpsi 550 kpsi	D882 D882
Elongation at Break	MD TD	180% 100%	D882 D882
Elmendorf Tear	MD TD	17 g/mil 14 g/mil	D1922 D1922
Spencer Impact		2.5 joules	
Transmission Rates	Oxygen Carbon Dioxide Water Vapor	675 cc-mil/m^2-24hr-atm 2,850 cc-mil/m^2-24hr-atm 375 g-mil/m^2-24hr-atm	D1434 Internal F1249
Optical Characteristics	Haze Gloss, 20°	2.1% 90	D1003 D1003
Thermal Characteristics	Melting Point	155-170°C	D3418

(1) Typical properties; not to be construed as specifications.

(2) All properties measured on 1.0 mil film.

(3) Typical values for a film oriented 3.5x in MD and 5x in TD.

Drying

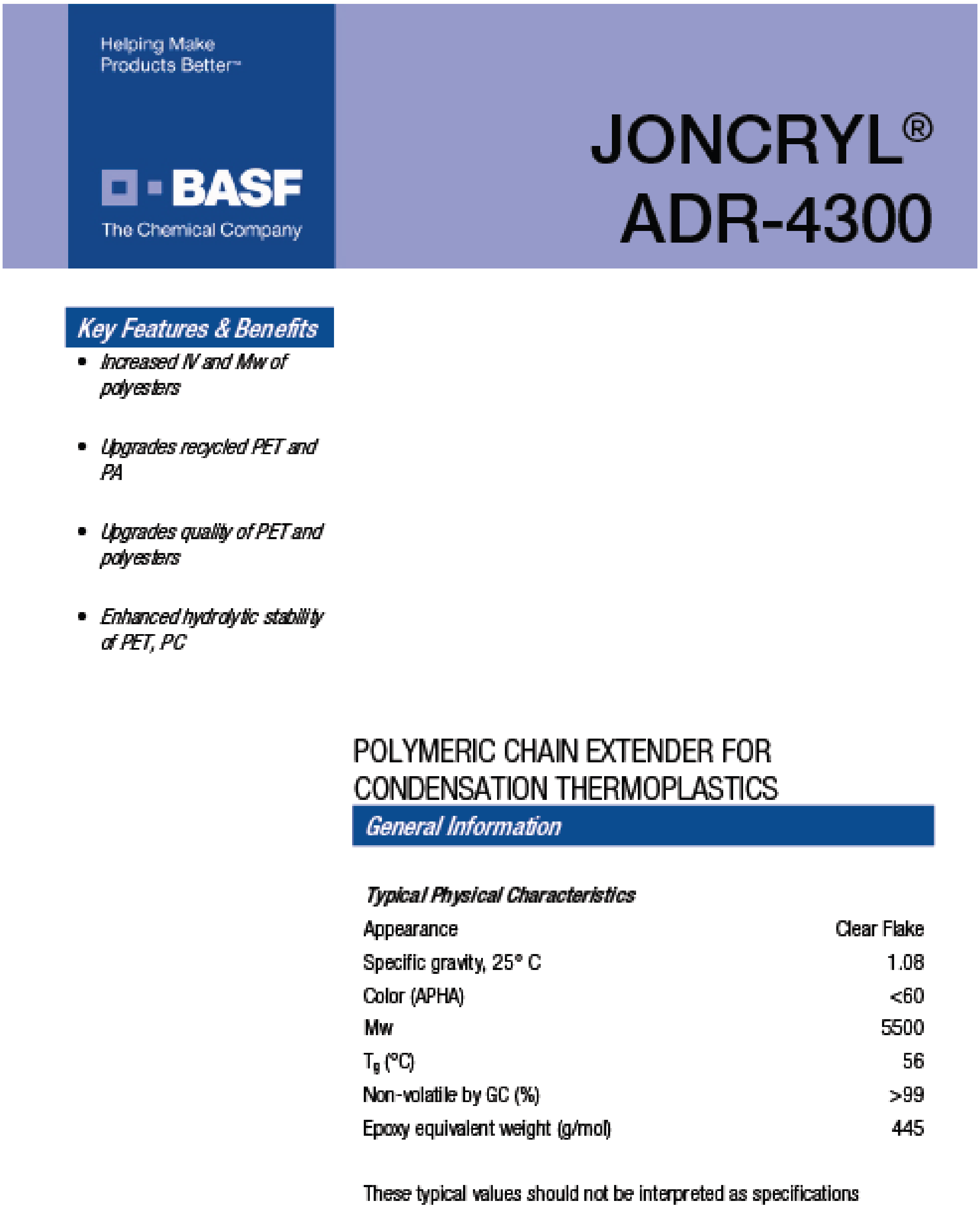
In-line drying is required. A moisture content of less than 0.025% (250 ppm) is recommended to prevent viscosity degradation. Typical drying conditions are 4 hours at 175°F (80°C) or to a dew point of -30°F (-35°C), with an airflow rate greater than 0.5 cfm/lb of resin throughout.

The resin should not be exposed to atmospheric conditions after drying. Keep the package sealed until ready to use and promptly reseal any unused material.

Processing Temperature Profile (1)

Melt Temperature	410 ± 15°F	210 ± 8°C
Feed Throat	113°F	45°C
Feed Temp.	355°F	180°C
Compression Section	375°F	190°C
Metering Section	390°F	200°C
Nozzle	390°F	200°C
Mold	390°F	200°C
Screw Speed	20-100 rpm	
Back Pressure	140-160°F	60-70°C
Mold Shrinkage	160-175°F	

A.2. BASF JONCRYL® ADR-4300 (SAmfE)



Helping Make Products Better™

BASF
The Chemical Company

JONCRYL®
ADR-4300

Key Features & Benefits

- *Increased IV and Mw of polyesters*
- *Upgrades recycled PET and PA*
- *Upgrades quality of PET and polyesters*
- *Enhanced hydrolytic stability of PET, PC*

POLYMERIC CHAIN EXTENDER FOR CONDENSATION THERMOPLASTICS

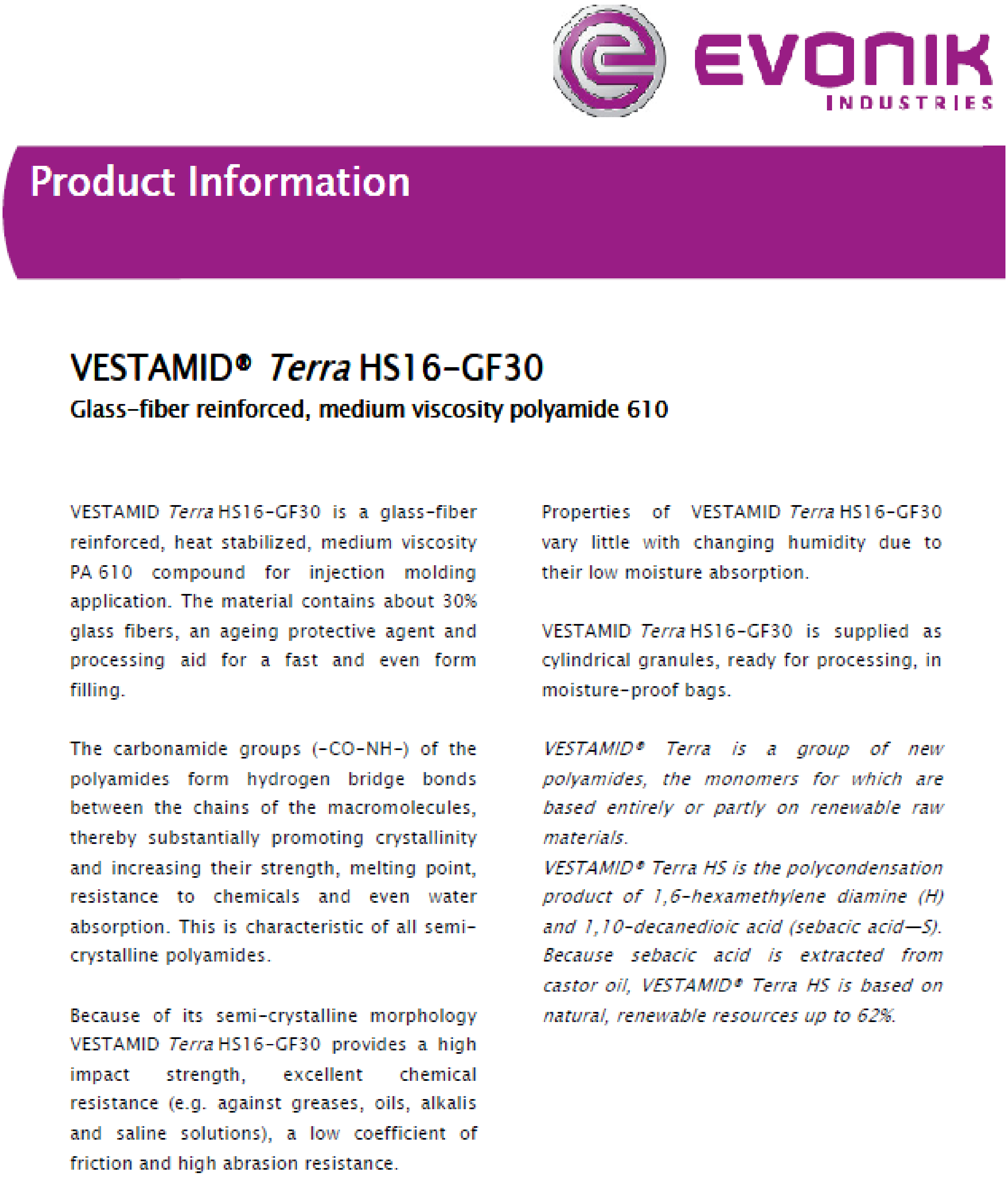
General Information

Typical Physical Characteristics

Appearance	Clear Flake
Specific gravity, 25° C	1.08
Color (APHA)	<60
Mw	5500
T_g (°C)	56
Non-volatile by GC (%)	>99
Epoxy equivalent weight (g/mol)	445

These typical values should not be interpreted as specifications

A.3. EVONIK VESTAMID® TERRA HS 16-GF30 (PA 610)



Product Information

VESTAMID® *Terra* HS16-GF30

Glass-fiber reinforced, medium viscosity polyamide 610

VESTAMID *Terra* HS16-GF30 is a glass-fiber reinforced, heat stabilized, medium viscosity PA 610 compound for injection molding application. The material contains about 30% glass fibers, an ageing protective agent and processing aid for a fast and even form filling.

The carbonamide groups (-CO-NH-) of the polyamides form hydrogen bridge bonds between the chains of the macromolecules, thereby substantially promoting crystallinity and increasing their strength, melting point, resistance to chemicals and even water absorption. This is characteristic of all semi-crystalline polyamides.

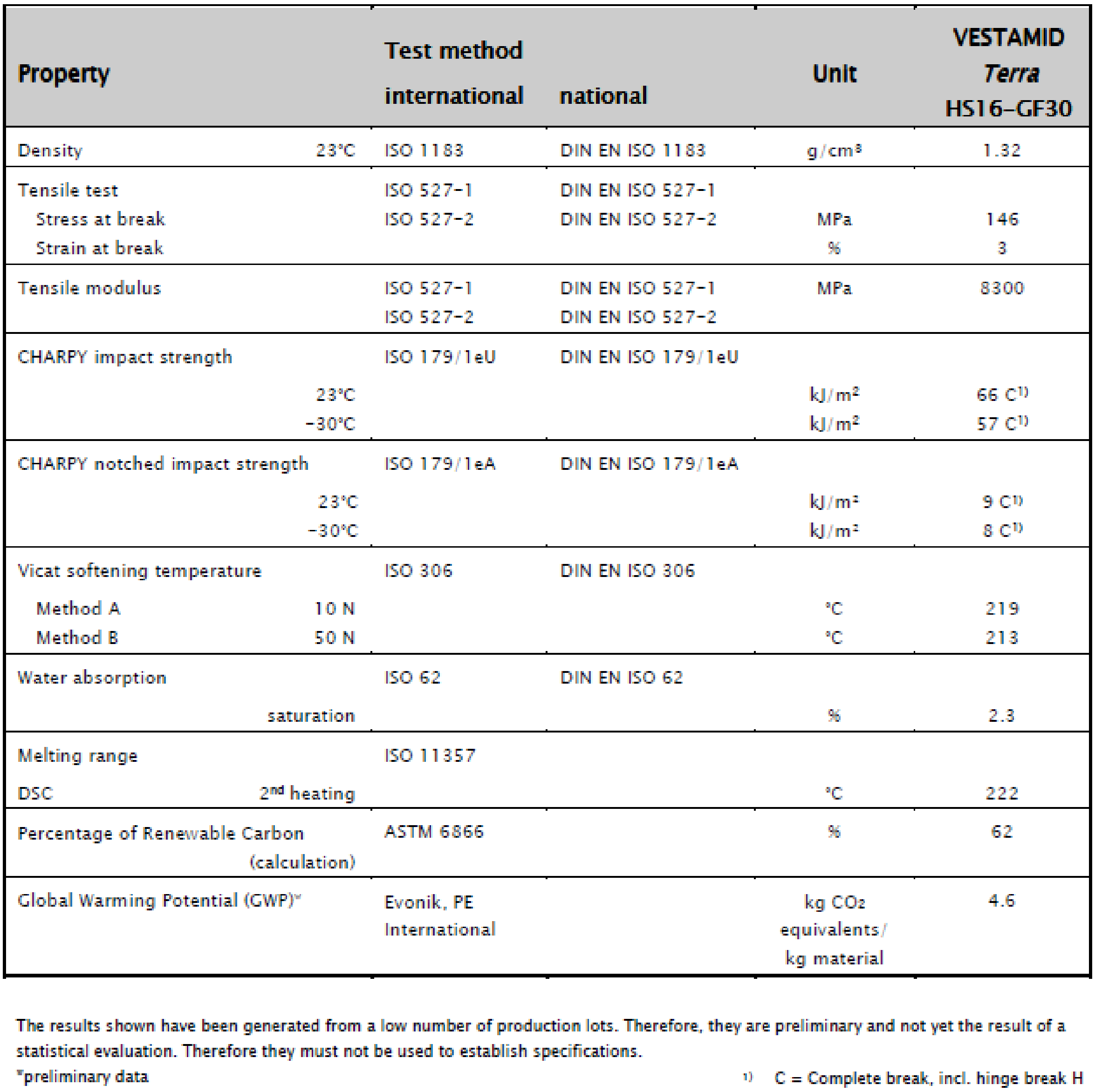
Because of its semi-crystalline morphology VESTAMID *Terra* HS16-GF30 provides a high impact strength, excellent chemical resistance (e.g. against greases, oils, alkalis and saline solutions), a low coefficient of friction and high abrasion resistance.

Properties of VESTAMID *Terra* HS16-GF30 vary little with changing humidity due to their low moisture absorption.

VESTAMID *Terra* HS16-GF30 is supplied as cylindrical granules, ready for processing, in moisture-proof bags.

VESTAMID® Terra is a group of new polyamides, the monomers for which are based entirely or partly on renewable raw materials.

VESTAMID® Terra HS is the polycondensation product of 1,6-hexamethylene diamine (H) and 1,10-decanedioic acid (sebacic acid—S). Because sebacic acid is extracted from castor oil, VESTAMID® Terra HS is based on natural, renewable resources up to 62%.



Property		**Test method** **international**	**national**	**Unit**	**VESTAMID** ***Terra*** **HS16-GF30**
Density	23°C	ISO 1183	DIN EN ISO 1183	g/cm³	1.32
Tensile test		ISO 527-1	DIN EN ISO 527-1		
Stress at break		ISO 527-2	DIN EN ISO 527-2	MPa	146
Strain at break				%	3
Tensile modulus		ISO 527-1 ISO 527-2	DIN EN ISO 527-1 DIN EN ISO 527-2	MPa	8300
CHARPY impact strength		ISO 179/1eU	DIN EN ISO 179/1eU		
	23°C			kJ/m²	66 C[1]
	-30°C			kJ/m²	57 C[1]
CHARPY notched impact strength		ISO 179/1eA	DIN EN ISO 179/1eA		
	23°C			kJ/m²	9 C[1]
	-30°C			kJ/m²	8 C[1]
Vicat softening temperature		ISO 306	DIN EN ISO 306		
Method A	10 N			°C	219
Method B	50 N			°C	213
Water absorption		ISO 62	DIN EN ISO 62		
	saturation			%	2.3
Melting range		ISO 11357			
DSC	2nd heating			°C	222
Percentage of Renewable Carbon	(calculation)	ASTM 6866		%	62
Global Warming Potential (GWP)*		Evonik, PE International		kg CO_2 equivalents/ kg material	4.6

The results shown have been generated from a low number of production lots. Therefore, they are preliminary and not yet the result of a statistical evaluation. Therefore they must not be used to establish specifications.

*preliminary data

[1] C = Complete break, incl. hinge break H

A.4. EVONIK VESTAMID® TERRA HS 16-GF30 (PA 1010)

EVONIK
INDUSTRIES

Product Information

VESTAMID® *Terra* DS16 natural color

Medium viscosity polyamide 1010

VESTAMID *Terra* DS16 natural color is a medium viscosity PA 1010 basic polymer. VESTAMID *Terra* DS16 is semi-crystalline, which is the reason for its high mechanical resistance and chemical stability. It absorbs only little water. As a result its mechanical properties vary little when exposed to changing environmental humidity, and the material features a high dimensional stability.

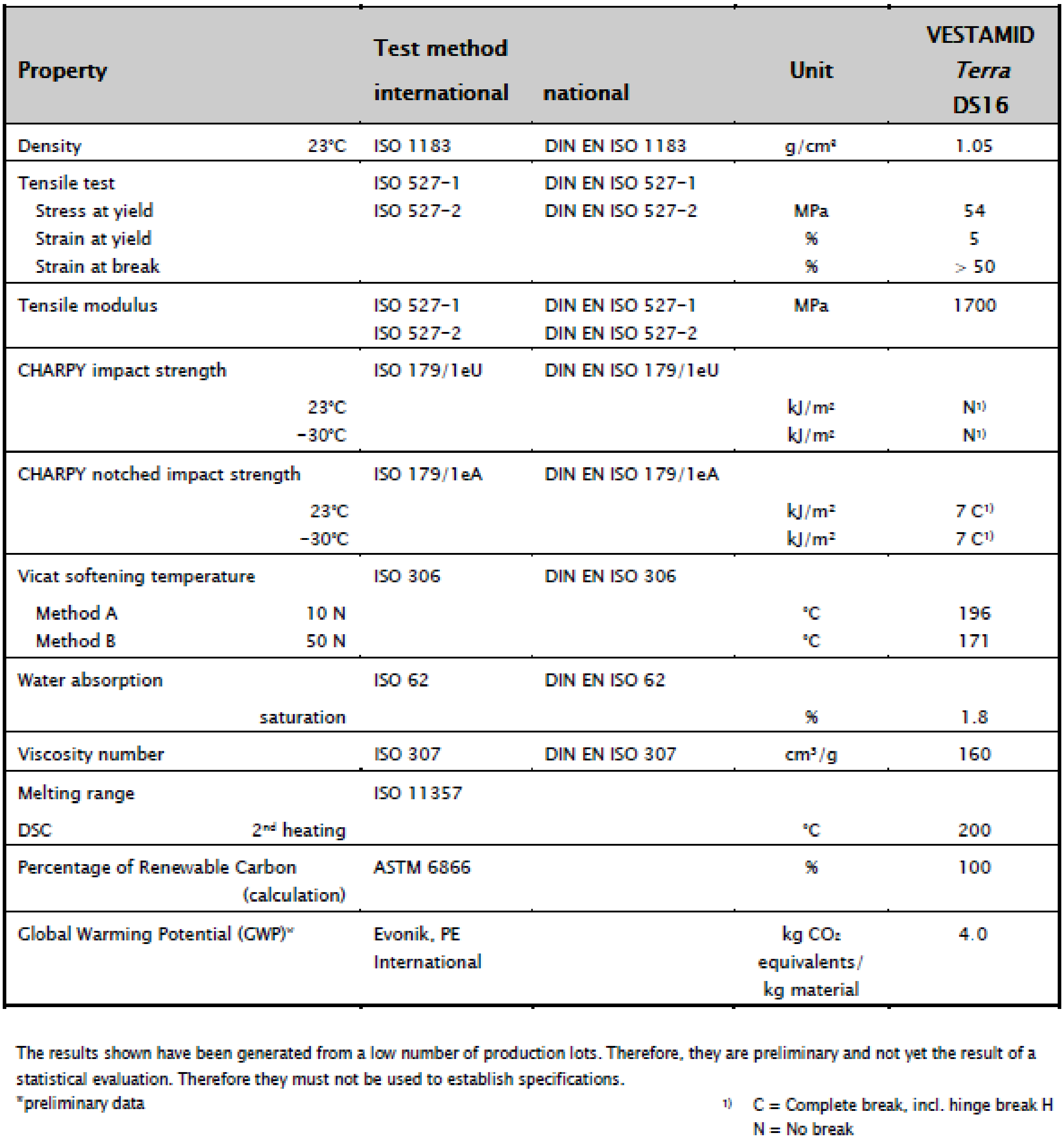
VESTAMID *Terra* DS16 can be used to manufacture films with good transparency.
The high melting point of VESTAMID *Terra* DS16 compounds results in a high heat deflection temperature that can be advantageous for some applications.

VESTAMID *Terra* DS16 occupies a position between the high-performance long-chain polyamides such as PA 12 and PA 1212 and the standard polyamides PA 6 and PA 66, which have a shorter chain length.

Because of its chemical and physical properties, and the plant origin of its monomers, VESTAMID *Terra* DS16 is an interesting addition to conventional longer-chain polyamides, and it also meets the growing demand for materials made from renewable raw materials.

VESTAMID *Terra* DS16 natural color is supplied as cylindrical granules, ready for processing, in moisture-proof bags.

VESTAMID® Terra is a group of new polyamides, the monomers for which are based entirely or partly on renewable raw materials.
VESTAMID® Terra DS is the polycondensation product of 1,10-decamethylene diamine (D) and 1,10-decanedioic acid (sebacic acid—S). Because both monomers are extracted from castor oil, VESTAMID® Terra DS is based on natural, renewable resources up to 100%.



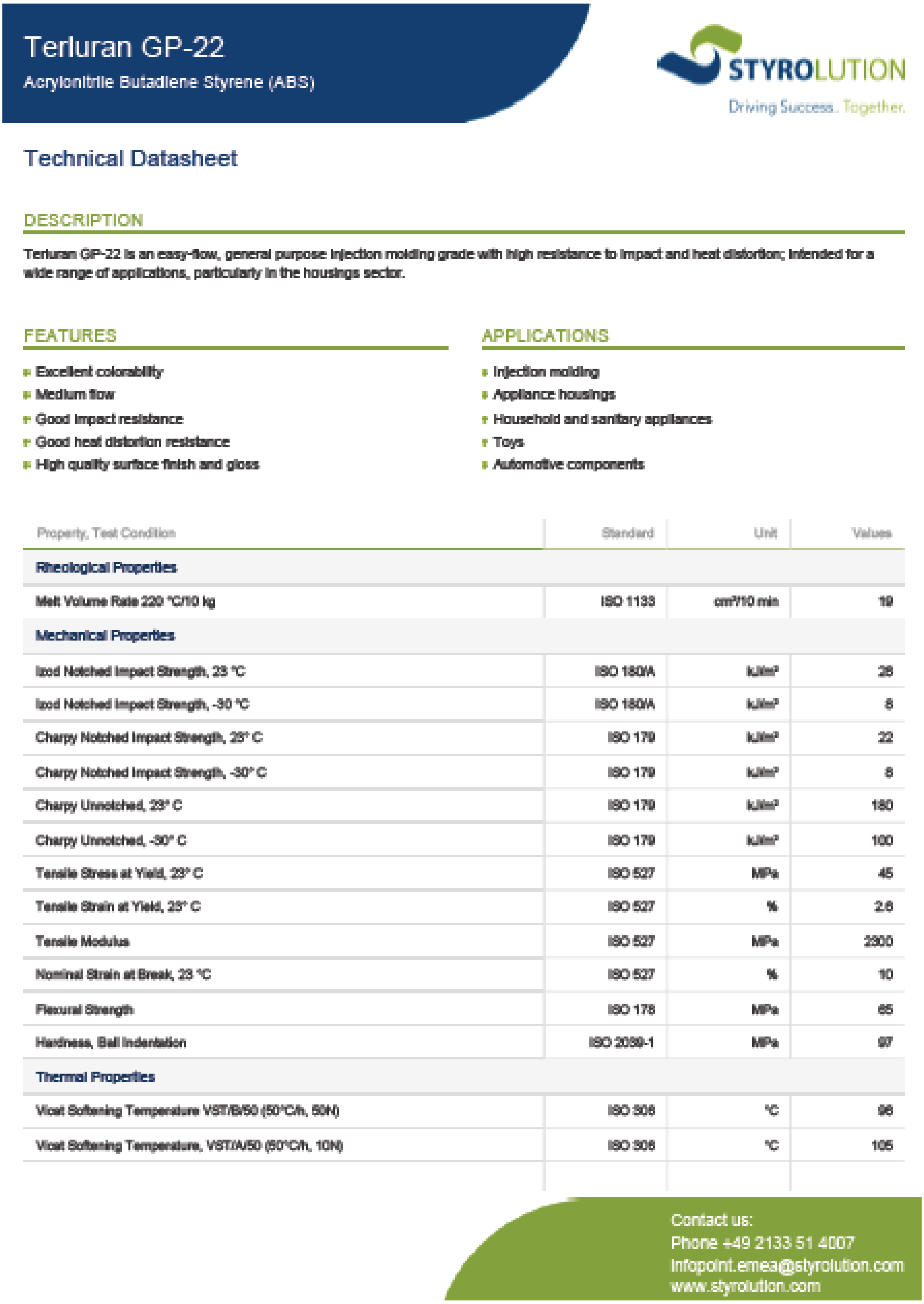
Property		Test method international	national	Unit	VESTAMID *Terra* DS16
Density	23°C	ISO 1183	DIN EN ISO 1183	g/cm^3	1.05
Tensile test		ISO 527-1	DIN EN ISO 527-1		
Stress at yield		ISO 527-2	DIN EN ISO 527-2	MPa	54
Strain at yield				%	5
Strain at break				%	> 50
Tensile modulus		ISO 527-1 ISO 527-2	DIN EN ISO 527-1 DIN EN ISO 527-2	MPa	1700
CHARPY impact strength		ISO 179/1eU	DIN EN ISO 179/1eU		
	23°C			kJ/m^2	N1)
	-30°C			kJ/m^2	N1)
CHARPY notched impact strength		ISO 179/1eA	DIN EN ISO 179/1eA		
	23°C			kJ/m^2	7 C1)
	-30°C			kJ/m^2	7 C1)
Vicat softening temperature		ISO 306	DIN EN ISO 306		
Method A	10 N			°C	196
Method B	50 N			°C	171
Water absorption		ISO 62	DIN EN ISO 62		
	saturation			%	1.8
Viscosity number		ISO 307	DIN EN ISO 307	cm^3/g	160
Melting range		ISO 11357			
DSC	2nd heating			°C	200
Percentage of Renewable Carbon	(calculation)	ASTM 6866		%	100
Global Warming Potential (GWP)*		Evonik, PE International		kg CO_2 equivalents/ kg material	4.0

The results shown have been generated from a low number of production lots. Therefore, they are preliminary and not yet the result of a statistical evaluation. Therefore they must not be used to establish specifications.

*preliminary data

1) C = Complete break, incl. hinge break H
N = No break

A.5. STYROLUTION Terluran GP-22 (ABS)



Terluran GP-22

Acrylonitrile Butadiene Styrene (ABS)

STYROLUTION

Driving Success. Together.

Technical Datasheet

DESCRIPTION

Terluran GP-22 is an easy-flow, general purpose injection molding grade with high resistance to impact and heat distortion; intended for a wide range of applications, particularly in the housings sector.

FEATURES

- Excellent colorability
- Medium flow
- Good impact resistance
- Good heat distortion resistance
- High quality surface finish and gloss

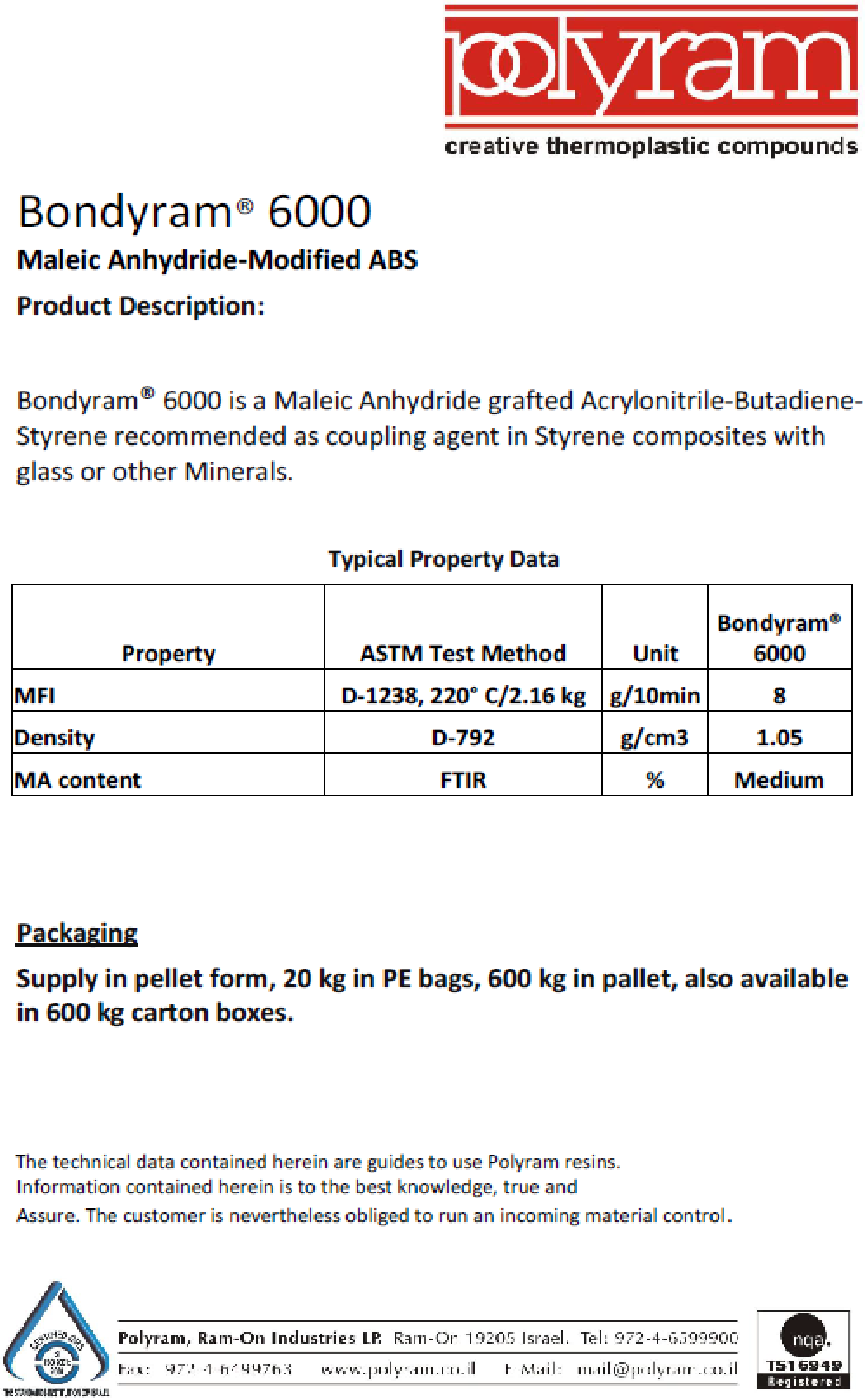
APPLICATIONS

- Injection molding
- Appliance housings
- Household and sanitary appliances
- Toys
- Automotive components

Property, Test Condition	Standard	Unit	Values
Rheological Properties			
Melt Volume Rate 220 °C/10 kg	ISO 1133	$cm^3/10$ min	19
Mechanical Properties			
Izod Notched Impact Strength, 23 °C	ISO 180/A	kJ/m^2	28
Izod Notched Impact Strength, -30 °C	ISO 180/A	kJ/m^2	8
Charpy Notched Impact Strength, 23° C	ISO 179	kJ/m^2	22
Charpy Notched Impact Strength, -30° C	ISO 179	kJ/m^2	8
Charpy Unnotched, 23° C	ISO 179	kJ/m^2	180
Charpy Unnotched, -30° C	ISO 179	kJ/m^2	100
Tensile Stress at Yield, 23° C	ISO 527	MPa	45
Tensile Strain at Yield, 23° C	ISO 527	%	2.6
Tensile Modulus	ISO 527	MPa	2300
Nominal Strain at Break, 23 °C	ISO 527	%	10
Flexural Strength	ISO 178	MPa	65
Hardness, Ball Indentation	ISO 2039-1	MPa	97
Thermal Properties			
Vicat Softening Temperature VST/B/50 (50°C/h, 50N)	ISO 306	°C	96
Vicat Softening Temperature, VST/A/50 (50°C/h, 10N)	ISO 306	°C	105

Contact us:
Phone +49 2133 51 4007
infopoint.emea@styrolution.com
www.styrolution.com

A.6. Polyram Bondyram® (ABS-g-MAH)



polyram
creative thermoplastic compounds

Bondyram® 6000

Maleic Anhydride-Modified ABS

Product Description:

Bondyram® 6000 is a Maleic Anhydride grafted Acrylonitrile-Butadiene-Styrene recommended as coupling agent in Styrene composites with glass or other Minerals.

Typical Property Data

Property	ASTM Test Method	Unit	Bondyram® 6000
MFI	D-1238, 220° C/2.16 kg	g/10min	8
Density	D-792	g/cm3	1.05
MA content	FTIR	%	Medium

Packaging

Supply in pellet form, 20 kg in PE bags, 600 kg in pallet, also available in 600 kg carton boxes.

The technical data contained herein are guides to use Polyram resins.
Information contained herein is to the best knowledge, true and
Assure. The customer is nevertheless obliged to run an incoming material control.

Polyram, Ram-On Industries LP. Ram-On 19205 Israel. Tel: 972-4-6599900
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Annex B: ISEB 2016 Conference – Poster presentation