Novel packaging films and textiles with tailored end of life and performance based on bio-based copolymers and coatings.

Report on the state-of-the art review

Written report including up to date literature (that will feed into review paper(s)), patent and commercial information on home compostable bio-based packaging and textiles among others

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List of abbreviations

AB	Advisory board
AD	Anaerobic digestion
BBI-JU	Bio-based Industries Joint Undertaking
Bio-PE	Bio-Polyethylene
BIF	Barrier improvement factor
CE	Circular economy
D	Deliverable
DA	Dicarboxylic acids
DP	Direct polycondensation
dtex	Diameter of the filaments
EC	European Commission
e-LCA	Environmental LCA
EoL	End of Life
EMS	Extrusion melt spinning
EVOH	Ethylene-vinylalcohol
FA	Fatty acid
FCM	Food contact material
FDCA	2,5-Furandicarboxylic
F&V	Fruits & Vegetables
HPLV	High performance liquid chromatography
HSI	Hyperspectral imaging
H2020	Horizon 2020
KMnO4	Potassium permanganate
KPI	Key performance indicator
LA	Lactic acid
LCA	Life cycle assessment
LCCA	Life cycle cost assessment
LCSA	Life cycle sustainability assessment
LD	Lactide
MA	Malic acid
MAP	Modified atmosphere packaging
MEG	Monoethylene glycol
MMT	Montmorillonite

MSW	Municipal Solid Waste
Mw	Molecular weight
MWCNT	Multiple walled carbon nanotube
NF	Natural fibres or fillers
NIR	Near infra-red
$nSiO_2$	Silica nanoparticles
OTR	Oxygen transmission rate
PBAT	Polybutylene adipate terephthalate
PBS	Polybutylene succinate
PDLLA	Poly(D,L-lactic acid)
PE	Polyethylene
PEF	Polyethylene furanoate
PHA	Polyhydroxyalkanoate
PLA	Polylactic acid
PLLA	Poly(L-lactic acid)
PPI	Pea protein isolate
PVOH	Polyvinylalcohol
P3HB	Poly(3-hydroxybutyrate)
REX	Reactive extrusion
ROP	Ring-opening polymerization
r-	Prefix for recycled (plastic)
SA	Succinic acid
s-LCA	Social LCA
SIRA	Strategic Innovation & Research Agenda
SPI	Soy protein isolate
s-PS	Syndiotactic polystyrene
SRM	Secondary raw material
TA	Terephtalic acid
TiO_2	Titanium dioxide
WVTR	Water vapor transmission rate
WPI	Whey protein isolate
WP	Work package
ZnO	Zinc oxide

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Executive summary

The conflicting objectives between reducing plastic waste that is of high demand by consumes and at the same time sufficiently protecting sensitive products forces industry and academic research to develop new sustainable packaging solutions. In this deliverable an extensive review of fundamentals and recent advances of bio-based packaging are outlined including innovative packaging, new materials and techniques for packaging and textiles, copolymers and modifications as well as processing and application scenarios.

Detailed insights are given into the composition, modification techniques and upscaling processes of bio-based film, multilayer, and fibre structures. Special emphasis was given to polyesters such as polylactic acid representing a promising bio-based film constituent. Modification and coating techniques of polylactic acid films as well as its biodegradation possibilities and monitoring parameters are summarized and discussed. Furthermore, protein-based films and multilayers especially from whey protein are extensively reviewed.

End of life aspects have also been surveyed in terms of processes and standards. All bio-based packaging material need to be fully examined starting from the use of raw material until its end of life option to determine its sustainability. Biodegradation processes and related key parameters and models describing degradation are outlined and discussed. Recent advances in sorting systems including detection methods and composting options as well as recycling possibilities provide knowledge about end of life options of bio-based packaging material. Furthermore, regulatory aspects are pointed out for each material, processing and end of life options.

This extensive review provides an overview of the current state of the complete life cycle of bio-based packaging. Up-to-date information including scientific articles, patents, and commercial information were summarized in order to provide a comprehensive overview of the most recent state of the art about bio-based packaging and textiles.

Introduction to D1.1

In the BIOnTOP project, the development of alternatives to conventional packaging concepts regarding sustainability criteria is the key aspect. This up-to-date review outlines the current achievements of bio-based packaging concepts including new material, material modifications, copolymers and multifunctional coating solutions. In addition, alternative routes to produce more sustainable packaging material are summarized such as routes to improve biodegradability, recycling properties and sorting processes. All the parameters are related to the sustainability of the packaging material.

Aim of D1.1

The aim of this deliverable is to provide the state of the art in order to compile all relevant and necessary information. This information is needed to advance the development of the new textile and packaging concepts in the further course of the project. This includes a market survey and benchmarking of existing solutions and in development state. In addition to the compilation of existing bio-based packaging concepts and research results, the biodegradability of the materials used has been on focus of the investigation. This task, which has been led by ASU, has been performed by the partners in their field and the results obtained will be used for a review article.

In an updated and more detailed fashion versus the related ambition chapter of the proposal, this deliverable will ensure each partner builds upon the actual state of the art when start developing their tasks and help highlighting the progresses beyond.

For the compilation of the required information, research is carried out in scientific literature (peer reviewed journals and magazines), patents and company brochures. The scientific literature was accessed from certain databases and websites. The references have been compiled using a literature management program. This up-to-date review provides a necessary tool to efficiently work on the BIOnTop project avoiding activities that were already done by others and at the same time using current knowledge for further research activities. Furthermore, a part or the complete deliverable shall be published in a scientific journal as extensive review article pushing the topic further in the academic literature.

Review of the state of the art in terms of bio-based packaging films and textiles as well as their biodegradation potential

1 Introduction

Plastic is most often the material of choice for packaging of food, cosmetics, or pharmaceutical products based on the excellent protection of the packaged product. In the last years, bio-based materials have been subjected to a strong growth for the sustainable packaging industry, due to the recent trends in the consumer market that have moved towards greener packaging and reduction of waste. Nowadays, the issue of sustainability is high, encouraging academia as well as industry to develop sustainable alternatives for preserving resources for future generations, focusing on biodegradable and bio-renewable materials.

To enhance the sustainability of packaging materials there are several ways. One way is to reduce the raw material needed by thinning the packaging film or by designing the packaging in a way that minimized the use of material. Both leads to lighter packaging and thus to a reduction in material resources, costs, and energy. (Amcor Sustainability Review 2018, 2018) Following this strategy, the amount of plastics, i.e. from fossil raw materials is reduced. Another way is to use post-consumer recycled material or to use refillable packaging e.g. PET bottles, thus enhancing the recycling of the packaging material. (Amcor Sustainability Review 2018, 2018; Geueke et al., 2018) Further enhancement in sustainable packaging was reached by using multilayer packaging. Multilayers combine lower amount of packaging material and improved barrier properties due to the use of several layers able to provide different barrier properties to protect the packaged product.

However, all the mentioned ways are limited and not suitable to obtain a packaging material that is completely sustainable and fulfils the requirements of a circular (bio)economy. For instance, multi layered packaging material has often a poor recyclability and thus, needs to be incinerated or even landfilled (Kaiser et al., 2018) Thus, there is a strong demand for bio-based material from renewable sources that are biocompatible and biodegradable. In general, bio-based plastics are defined as man-made or man-processed organic macromolecules derived from biological resources. (Harish Prashanth and Tharanathan, 2007) Amongst the plastic produced annually, only 1 % represents bio-based plastics in Europe. (European Bioplastics) It is to be highlighted that the demand for bio-based materials for packaging is expected to grow up to 9.45 million tons by 2023. (Bajpai, 2019)

Innovative packaging material composed of blends or pure bio-based material is suitable to improve sustainability aspects. Using renewable resources for the development of bio-based packaging material shall provide a lower carbon footprint, reduces the environmental impact (Amcor Sustainability Review 2018, 2018), acceptance by consumers, maintains barrier properties and self-life of the packaged good, and provide a sustainable end-of-life. (Thielen, 2012) Innovative packaging concepts include novel materials, mono or multilayers, as well as their biodegradability. Novel materials to be used for bio-based packaging shall be biocompatible and biodegradable as well. Bio-based sustainable packaging material shall be ideally derived from renewable resources or side streams from processing of agricultural or food products that are gaining high attention in industry and academia. For instance, whey proteins, a side stream product of cheese processing, has been already extensively studied as packaging material. (Bugnicourt et al., 2013; Cinelli et al., 2014; Schmid, Benz et al., 2012; Schmid, Dallmann et al., 2012; Schmid and Müller, 2019; Zink et al., 2016) The detrimental barrier properties of whey protein-based films can be overcome by physical modification of proteins to tailor their properties. Physical modifications include heat treatment (Hong and Krochta, 2006), ultrasonic treatment (Zhou et al., 2009) or irradiation (Ustunol and Mert, 2006) of proteins to create protein films and coatings. Recent developments were obtained in chemical modification of proteins especially by chemical grafting using fatty acids to improve the water vapour barrier properties. (Samain, 2002) Besides whey proteins, also proteins from soy and peas (Chang et al., 2019) as well as polysaccharides such as cellulose and starch (Hu, 2014; Simon, 2011) have been analysed regarding their packaging film properties.

Among proteins and polysaccharides, polyesters are also extensively studied polymers from biomass. Polyesters such as polyethylene furanoate or polyhydroxyalkanoate are bio-based and suitable for various packaging applications. To use these newly developed material for large-scale production, recent developments in processing and upscaling of bio-based material are outlined in this review. (Cambridge Consultants, no date)

Polylactic acid (PLA) is one of the most studied synthetic bio-based polymers already applicable for various industrial packaging applications. PLA-based packaging material can be modified by copolymers of compounds that influence its flexibility. (Blasi, 2019; Perinelli et al., 2019; Sharma et al., 2019)

The subject of this review is to illustrate the current state-of the art about bio-based packaging and textiles as well as modification strategies and application scenarios. To fully assess the sustainability of bio-based packaging material, the evaluation of different end-of-life options including home and industrial composting are outlined and discussed in this review. In the end, recent advances in the development of bio-based packaging material for specific applications are demonstrated.

2 Types of bio-based and innovative packaging

In contrary to “bio-based plastics” that are made of renewable raw materials the term “bioplastics” is used in the academic literature to describe both plastics that are bio-based and/or plastics that are biodegradable. Bio-based polymers used in packaging are available from renewable raw materials, that usually are also biodegradable and/or biocompatible. Polymers that are biodegradable describe materials that degrade completely when exposed to microorganisms, in aerobic or anaerobic processes. In contrary, biocompatibility has several definitions, however, in fact biocompatibility describes the ability of materials to be compatible with biological material, be in harmony with tissue, and to obtain no toxic nor injurious effects on biological systems. (Thomas et al.)

Nowadays, designing and manufacturing of packaging products must meet specific sustainability criteria, which are related to the harmony of economic, social as well as environmental developments.. An overview of biodegradable polymers feasible for packaging material is given in **Figure 1**. In addition to the Biopolymers outlined in **Figure 1**, waxes and lipids are also studied as bio-based packaging constituent. (Pérez-Gago and Krochta, 2001)

Bio-based plastics are made of carbon compounds. The carbon-based compounds occur either naturally or may be produced through photosynthesis from natural components such as cellulose, hemicellulose, lignin, plant oil or being extracted from corn, sugarcane or other biomass. Alternatively, the carbon-based compounds can be synthesized from bio-derived monomers via polymerization processes, such as poly(lactic acid) (PLA) or bio-polyethylene (bio-PE) (Mielcarek.O and Masek.A, 2019). A third option bio-based plastics can be produced is from microorganisms, for instance, polyhydroxyalkanoates, xanthan, or pullulan (**Figure 1**). (Gabor and Tita, 2012)

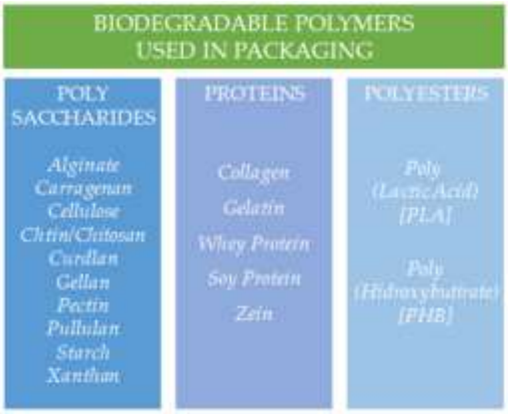


Figure 1 Biodegradable polymers used in packaging (adapted by (Gabor and Tita, 2012))

Significant efforts have been made to identify new resources for bio-based plastics, such as non-food materials of agricultural crops, to produce packaging materials. These alternative materials have attracted considerable interest in research for a long time. In recent years, these materials have reached the market. Moreover, technological progress such as those based on nanotechnology are promising techniques suitable to improve bio-based polymer properties and increasing the number of potential applications for such materials in packaging. (Bajpai, 2019)

2.1 Traditional Packaging

Packaging can be defined as material, which does not affect the packaged product. This means, the packed product shall be protected from the environment that means from light, oxygen, water, chemical and microbial contamination by the packaging material. In addition, the packaging material shall provide flexibility, thermal stability, good mechanical and optical properties, resistance to chemicals and to UV radiation. (Bajpai, 2019; Gabor and Tita, 2012) Moreover, product packaging serves as an effective means of marketing to communicate with the consumer. The design of packaging can vary in shape and size and, is used as a user interface to provide consumers with both product information as well as convenient handling. Overall, the main functions of packaging can be summarized to protection, communication, convenience and containment. (Schaefer and Cheung, 2018)

With the word packaging, different target materials may be involved leading to the need to divide packaging in three groups based on its purpose: (Bajpai, 2019)

- Food packaging
- Non-food packaging
- Food service packaging

Based on the packaging purpose, different characteristics are required. General requirements for packaging are reported in this chapter while an in-depth analysis regarding the specific application is outlined in **chapter 8.1** for non-food packaging and **chapter 8.2** for food packaging.

Materials designed for packaging, especially the ones related to food industry, need to comply with strict criteria. Above all, packaging material cannot have a negative impact on human health or life. (Mielcarek.O and Masek.A, 2019) In addition, the main material requirement for food packaging is the feasibility of the material for food contact. The European commission announced substances that are allowed to be used in food contact. (European Commission, 2004, 2011) The packaging material available to be used in food contact need to meet the following criteria: The material remains unchanged by contact with aqueous, acidic and fatty foods at or below room temperature and even at temperature as high as 60 °C. (Siracusa et al., 2008) Another important feature of food packaging is that the material shall present organoleptic properties that are as neutral as possible (clear, transparent, odourless, tasteless etc.) in order to not be detected when eaten and consequently modify the organoleptic properties of the packaged food. (Guilbert and Contard, 2005)

2.1.1 Edible films

In contrast to traditional packaging material, there are also edible packaging materials. Edible films for packaging are produced in thin layers using wet or dry manufacturing processes. The resulting film should be a free-standing sheet that may be used between food components for separation purposes or over the food as wrapping or packaging. In contrast to edible films, edible coatings are materials which can be applied directly to the surfaces of food products by dipping, spraying or panning. Edible coatings can be consumed with the food product directly. (Kadzińska et al., 2019; Yu et al., 2018)

To overcome these drawbacks, recent studies focused on the use of nanomaterials added to the edible film polymers to enhance their properties as packaging material. (Kozitsina et al., 2018) Researchers studied the effect of nanomaterials (particles containing less than 100 nm in at least a dimension of its size) such as zinc oxide (ZnO), titanium dioxide (TiO_2), magnetic iron, aluminium, copper, silver, cerium oxide, and silica nanoparticles ($nSiO_2$), in addition to single or multiple walled carbon nanotubes on the properties of edible film polymers. Nanomaterials have been used in polymers to produce enhanced rigid, biodegradable and/or flexible packaging materials. Polymeric nanocomposites have been developed for multi-layered application in packaging of carbonated beverages, bottling beer, and thermo-formed containers, where the middle layer is reinforced with a nanocomposite film with improved barrier attributes. (Barik and Badamali, 2017; Xie et al., 2018)(Müller et al., 2017) For more details please see **Chapter 6.5**.

2.2 Innovative Packaging

Traditional packaging does often not meet the requirements of actual trends such as customers experience expectations and products complexity as well as national and international initiatives to promote minimization of carbon footprint of manufactured products and circular economy. (Schaefer and Cheung, 2018) Thus, in the last years, innovative packaging with enhanced functionalities has been developed and new terms have emerged to identify them. Innovative packaging is subdivided into the terms intelligent packaging, active packaging and smart packaging:

- **Intelligent packaging** (**chapter 2.2.1**) is defined as “a packaging system that is capable of carrying out intelligent functions (such as detecting, sensing, communicating, recording and tracing) to facilitate decision-making to extend shelf life, improve quality, enhance safety, provide information and warn about potential problems” (Otles and Yalcin, 2008)
- **Active packaging** (**chapter 2.2.2**) is defined as “a packaging system with the aim of maintaining or extending product quality and shelf-life” (Idumah et al., 2019; Vanderroost et al., 2014)
- **Smart packaging** describes packaging that combines intelligent and active packaging. Smart packaging is defined as “a total packaging solution that on the one hand monitors changes in a product or its environment (intelligent) and on the other hand acts upon these changes (active)”. (Vanderroost et al., 2014)

Results presented by Rodríguez-Rojas et al., 2019 show that scientific attention drastically moved towards intelligent and active packaging, where “Antimicrobial packaging” and “Active Packaging” have been the most used keywords in academic publication’ titles over the last years. Innovative packaging has huge potential in the sector; however, it is well known that waste generated by innovative packaging is mostly unable for recycling. (Da Cruz et al., 2014) Thus, one of the main challenges in the design and manufacture of innovative packaging is the development of new materials that are able to be recycled. (Schaefer and Cheung, 2018)

2.2.1 Intelligent Packaging

Intelligent and smart technologies are often tailored to be used in monitoring the status of packaged material, such as freshness or environmental conditions surrounding the package. Intelligent solutions have been used to detected changes in a product or its environment, for example changes in temperature, pH level or humidity. The main requirement necessary for intelligent packaging material is the compatibility with the packed product, the costs and the robustness. (Idumah et al., 2019) It is important to report that technologies for intelligent packaging solutions are not limited to material developments but also to digital technologies, as for example augmented reality. The authors wanted to highlight this aspect, but as it exceeds the scope of this work we refer to other sources on the topic. (Guo and Du, 2017; Li and Si, 2019; Schaefer and Cheung, 2018)

In the food packaging sector, biosensors have been used to individuate, record and communicate information regarding potential spoilage that may have occurred in the package or changes in oxygen content or freshness level. (Bott et al., 2018; Kumar et al., 2018a; Yousefi et al., 2019) (Müller and Schmid, 2019) Nanomaterials are most often in use for biosensors on packaging material. Biosensors based on nanomaterials revealed excellent properties presenting faster, cheaper and easier solutions compared to established technologies such as high-performance liquid chromatography (HPLV), fluorescence, etc. (Idumah et al., 2019) In literature, biosensors developed on colorimetric and optoelectronic technologies as well as enzymatic, oxygen or dye-based sensors are reported. (Mohebi and Marquez, 2015) Neethirajan et al., 2018 investigated an ultraviolet-based colorimetric oxygen indicator using TiO_2 nanoparticles that have been used in polymer encapsulating system in the presence of methylene-blue and tri-ethanolamine. The sensor undergoes bleaching and maintains a colourless state when UV-irradiated, but on exposure to oxygen, it returns to its original blue colour communicating that the atmosphere of the package is not controlled anymore and the freshness of the product cannot be ensured. (Neethirajan et al., 2018) Use of bio-based sensors in meat was reported by Huang et al., 2014 who studied a colorimetric gas sensor from black rise natural extracts for sensitive detection of amines generated in pork meat during the gradual decomposition process. The sensor detected carbonyl and hydroxyl groups of anthocyanin molecules in the black rice extract that reacted with amines generated during meat spoilage. (Huang et al., 2014)

In conclusion, future expectations on intelligent packaging relies on the development of sensor technologies and materials to inform about its quality, safety, shelf life and usability. Schaefer and Cheung, 2018 tried to individuate future aspects about intelligent packaging and reported that the possible targets of future investigations will be:

- Enhancement of sensor technology in order to incorporate innovative packaging solutions in conventional materials
- Development of new sensor for recycling purposes of innovative packaging materials and food wastes
- Integration of innovative packaging in digital and production network in the context of Industry 4.0

Intelligent packaging is supposed to get in contact with food which is regulated by the EU regulation 450/2009. In this regulation intelligent packaging is described as packaging that informs consumers about the state of a food product. Intelligent systems such as biosensors are usually placed on the surface of the package and be separate from the food inside to inhibit migration towards the food product ensuring the safety of intelligent packaging. (EU Verordnung (EG) Nr. 450/2009, 2009)

2.2.2 Active packaging

Active technologies are tailored by the inclusion of specific constituents in the packaging material. They depend on chemical, physical or biological actions that modify the interactions between the package, the product and/or the headspace inside the package. (Bajpai, 2019) Active packaging was born as an answer to continuous changes in consumer demands and market trends. The advantages of active packaging technology lies in the reduction of the quantity of active substances needed, in the migration of particles into the substance packaged as well as elimination of unnecessary industrial processes that can be responsible for the introduction of bacteria into the product. (Schaefer and Cheung, 2018) The goal of active packaging is to enhance the preservation of food in the package and prolonging its shelf-life. In contrary to intelligent packaging, active packaging directly influences the packaged product by adding or scavenge substances to/from the food product. (EU Verordnung (EG) Nr. 450/2009, 2009) Active packaging involves application of various strategies like temperature or moisture control, oxygen absorption, ethylene scavengers, addition of flavour and odour absorber/releaser as well as substances capable to release antimicrobial agents, CO_2, or flavours. (Biji et al., 2015; Wilson et al., 2018); (EU Verordnung (EG) Nr. 450/2009, 2009)

Antimicrobial packaging is the main and foremost-investigated application of active packaging, it is based on the reduction, inhibition and delay of microorganism growth that may be present in the packaged product. It may involve applications by incorporation or by coating of the active agent and it is widely used in the food industry where has received strong interest for the development of meat, fish, poultry, bread, cheese, fruits, and vegetables packaging. (Kenyó et al., 2018) A widely known system used in industrial application is the “BioSwitch” technology, where an antimicrobial agent is released on command when the packaging environmental conditions change, for examples in response to bacteria growth. Typical materials used for antimicrobial purpose are silver ions, ethyl alcohol, chlorine dioxide, allyl isothiocyanate, nisin, organic acids, essential oil and metal oxides, (Bajpai, 2019) as well as polylactic acid (PLA) or polybutylene adipate terephthalate (PBAT) nanocomposites based on metal, metal oxides, organo-modified nano-clays, natural biomaterials, enzymes and synthetic antimicrobial materials. (Kumar et al., 2018b) Moisture control is another cause of product spoilage that is based on the water activity in the product, which leads to microbial growth. Moisture control solutions for packaging are classified into two categories: (Idumah et al., 2019)

- **Passive**, by the replacement of the humid air in the headspace with dry gasses and consequent use of packaging material with water barrier properties
- **Active**, by the application of desiccant/water absorber agents that can scavenge water molecules inside the package

The desiccants absorption capacity depends on its water vapour sorption isotherm and commonly it is positioned in packages in the form of microporous bags, sachets, or integrated into pads. Also drip absorbent sheets are used, which are constituted of two layers of microporous polymer, like polyethylene or polypropylene, sandwiched with a superabsorbent polymer. (Biji et al., 2015) Typical desiccants used in moisture control applications are clays, silica gel, zeolites, calcium oxide and molecular sieves that are capable to control humidity in the packaging headspace. (Idumah et al., 2019)

Gas scavenging, or emission, is a widely investigated application for active packaging technologies due to the many gasses that can affect packaged stuff:

- **Ethylene gas**, it is known to speed up the maturity of fruit being a plant-ripening hormone that presents physiological influence on vegetables and fresh fruits. (Janjarasskul and Suppakul, 2018)
- **Volatile aldehydes and amines**, which are known to form during food degradation, may change the flavour and odour of the product. (Biji et al., 2015)
- **Oxygen gas**, which promotes several undesired effects such as formation of off-flavours and odours, growth of aerobic microorganisms, changes in colour, reduction in shelf-life (Bajpai, 2019). It also influences the production of ethylene in fruits and vegetables. (Biji et al., 2015; Idumah et al., 2019)

Different solutions have been developed for each gas involved. Issues on ethylene scavenging have been solved by use of potassium permanganate ($KMnO_4$), which is the main material used in packaging application thanks to an oxidation process that reduce the olefinic gasses. It is generally immobilized on inert minerals such as nano-clays, activated alumina, silica gels, vermiculite or zeolites. Besides $KMnO_4$, carbon bases with metal catalysts, activated clays (zeolites), trienes and silicon polycarbonates are also known and commercially used for ethylene scavenging. (Biji et al., 2015; Idumah et al., 2019)

For flavour and odour control, it must be taken into account that these scavengers are not allowed in the European Union, indeed odour is the main detection method for consumers to evaluate the product quality. Thus, there are issues that the removal of flavouring agents may lead the consumer to consider the food to be consumed. (Bajpai, 2019) When applied, this application uses materials such as synthetic aluminosilicate zeolites, D-sorbitol, cyclodextrin, sodium or organic sulphates to remove selectively aldehydes, while amines formed due to protein breakdown can be removed by the use of citric or ascorbic acid. (Bajpai, 2019)

Oxygen scavenging is surely the most studied application of gas control in active packaging. Indeed, even if oxygen is previously removed in the package and superior barrier packaging solution are adopted by use of multi-layered structures or barrier nanocomposites, this traditional packaging technique does not grant complete removal of oxygen and cannot prevent possible dissolution of oxygen inside the food. (Lee et al., 2018; Yang et al., 2018)

Active packaging techniques can solve this issue minimizing the presence of oxygen residues in the package by the use of oxygen scavengers, which are designed to reduce oxygen content below 100 ppm in package headspace. These are commonly used as small sealed sachets and added to the package, generally constituted of iron-based powders, which react with the water provided by the food to produce a reactive hydrated metallic reducing agent that scavenge oxygen within the food package. However, issues about this technology are reported due to the risk of incidental ingestion and recycling issues. (Biji et al., 2015; Idumah et al., 2019)

Nanomaterials and polymer nanocomposites are under development as possible alternative solutions to these issues. For example, Galstyan et al., 2018 investigated the photocatalytic mechanism under ultraviolet radiation of nanocrystals of titanium oxide (TiO_2) which could possibly be used as oxygen scavenger. Similarly, Lee et al., 2018 developed an oxygen scavenger based on activated carbon and sodium L-ascorbate for application in raw meatloaf.

Finally, an interest has been developed in packaging technologies for the use of CO_2, which is directly correlated with O_2 removal. Indeed, oxygen elimination leads to vacuum formation inside the package which can collapse flexible structures. Mechanisms for release of oxygen consuming CO_2 has been developed by the use of ferrous carbonate or a combination of sodium bicarbonate and ascorbic acid. (Gorrasi et al., 2017) Nevertheless, absorbers are needed in order to find an equilibrium in the packaging pressure and avoid package breakage due to high presence of CO_2 gas. Calcium, potassium/sodium hydroxides, calcium oxide and silica gel are typical materials used as CO_2 scavenger. (Idumah et al., 2019) Recently, nanoporous crystalline syndiotactic polystyrene (s-PS) has been individuated as an excellent material for CO_2 absorption purposes in fruit packaging, attributing its properties to gas diffusivity and structure orientation. (Rizzo et al., 2018)

3 Textiles - Material and techniques

3.1 Bio-based textile material

The term “textile” refers to natural or synthetic fibres, filaments and yarns. These are characterised by their length, dimensionality and structure. While fibres and yarns usually are one-dimensional, fabrics appear two or three dimensional. A fibre is a raw material of textile, which can be characterized by flexibility, fineness and ratio of length to thickness. If the fibre runs continuously, it is called a filament. Filaments are characterized by their ratio of length to weight. In contrast, a yarn is the combination of several layers of fibres and filaments. (Lomov et al., 2005)

Currently only small parts of biodegradable materials are used for textile applications, which are incorporated into oil-based polymers. Examples are Bio-PE, Bio-PET or Bio-poly trimethylene terephthlate. Bio-based polyethylene terephthalate is a chemically identical plastic to conventional PET in which a petrochemical component is replaced by a bio-based one. (Ruys and van Olmen, 2012)

Conventional PET consists of 70% terephthalic acid (TPS) and 30% monoethylene glycol (MEG). For bio-based PET, the MEG is used instead of fossil fuels from renewable plant raw materials. Nevertheless, Bio-PET is ecologically controversial. Agricultural land is needed to enable production of renewable plant materials in large quantities. In addition, the bio-based PET packaging or PET in general can only be degraded by very specific microorganisms such as *Ideonella sakaiensis 201-F6* (Yoshida et al., 2016). However, to what extent PET is biodegradable or compostable seems to be still controversial. (Yang et al., 2016)

In addition to oil-based polymers, biopolymers show great potential in the production of textiles. Many of these polymers can be used to produce fibres and fragments that can completely or partially replace petroleum-based polymers due to their similar properties. For many years, investigations have been underway about biopolymers in order to replace oil-based polymers e.g. for packaging material. We need to point out that polymers differ in their properties and can be obtained in different ways that both strongly influence the ability of biopolymers to be used as fibres and fragments. For instance, biopolymers can be obtained directly from natural substances that include polysaccharides and proteins. Alternatively, biopolymers can be prepared by polymerization such as PLA (**chapter 5.1**,**chapter 3.1.15.1**) and other polyesters that are made from monomers and others can be produced by microorganisms such as polyhydroxyalkanoates (PHA) (**chapter 3.1.2**) (Blackburn, 2009)

In the following the most promising biopolymers for textile packaging applications are outlined.

3.1.1 Polylactic acid (PLA)

Fibres made of PLA show the highest potential to be used as raw material for textiles because they are very similar to other thermoplastics because of their smooth surface and the low moisture regain. PET is closest to PLA due to its similar mechanical properties. PLA fibres are made of a fermentable sugar, such as dextrose from corn starch. (Drumright et al., 2000) PLA fibres have a smooth surface and a relative density below that of PET. However, PET and PLA obtain similar mechanical properties. Similar to PET filaments, PLA filament yarns and spun yarns can be used to produce fabricates. These yarns are convincing due to their low moisture absorption and fast drying. Compared to PET, PLA revealed significantly better results in terms of flammability. The smoke emission as well as the duration of the further burning after removal of the flame is lower for PLA filaments compared to PET fibres. In addition, the PLA fibres do not absorb UV light that is in contrary to petroleum based fibres, which in turn led to decrease in tensile strength of PLA fibres when exposed to UV light. (Cinelli et al., 2014; Nurul Fazita et al., 2016)

3.1.2 Polyhydroxyalkanoate (PHA)

Similar to PLA, PHA reveals high potential to replace petroleum-based materials. (Bugnicourt et al., 2014a) PHA is obtained by bacteria. The microbial production of the PHA takes place in several steps, whereby the properties can be adjusted by the substrate and the fermentation conditions. (Chen, 2009) Advances in molecular and genetic engineering led to an increase in bacterial strains able to produce PHA, such as *Ralstonia Eutropha* or *Alcaligenes Latus* (Bugnicourt et al., 2014a).

The use of plasticizers such as glycerol and the combination with other copolymers enhances the flexibility and process capability of PHA as packaging material, PHA can be either used with a high or low molecular mass depending on the application. For thermoforming or blow moulding, PHA with a high molecular mass is suitable and offers improved mechanical properties compared to low molecular weight PHA. PHA with low molecular mass are suitable for injection moulding applications. (Nagarajan et al., 2016) Overall, PHA packaging material provides higher mechanical strength than PLA material. (Bugnicourt et al., 2014a)

3.1.3 Polybutylene succinate (PBS)

PBS is a polyester formed by polycondensation. PBS has high crystallinity and good thermal properties, with mechanical properties similar to those of PP. (Xu and Guo, 2010) While PBS was produced for a long time with the help of petrochemical materials, bio-succinic acid can be synthesized by yeasts or bacteria such as *Anaerobiospirillum succiniciproducens* as patented previously. (5,573,931) For example, pots made of PP can be replaced by using pots made of PBS nonwovens. (Siwek et al., 2013) In addition, PBS can be used as an additive for plasticizing other bio-polymers such as PLA. (Jompang et al., 2013)

A recently published patent describes a new material composed of a PBS and PLA as laminates. These laminates can be produced by several methods, such as in an extrusion coating process. By using this combination to produce fabrics, the laminates offer the advantage of higher biodegradability in the presence of bacteria. (JP3216909U)

3.1.4 Polyethylene furanoate (PEF) and 2,5-Furandicarboxylic acid (FDCA)

PEF is made of FDCA and MEG. PEF which is produced by polymerization, has the potential to push conventional PET off the market. In comparison to PET, PEF is completely biodegradable and provides enhanced mechanical and barrier properties: PEF material provides a higher tensile strength and it has the advantage of being processed at low temperatures which leads to energy saving. In addition, the barrier properties such as the protection against oxygen, carbon dioxide and water vapour is considerably higher by PEF than by PET (see **chapter 4.1** for more details). Bottles, fibres and films made of PEF are commercially available. (Avantium, no date b)

FDCA is a monomer derived from sugars using biofermentation. FDCA fulfils the task to replace oil-based terephthalic acid (TA) during production of PET to produce PEF. Furthermore, FDCA offers the possibility to produce other polymers such as polyesters, polyamides and polyurethanes as well as coating resins, plasticizers and other chemical products. (Avantium, no date b)

3.1.5 Cellulose and Nanocellulose

Cellulose, a polysaccharide, is one of the most commonly used biopolymers for alternative natural packaging material. Cellulose is composed of *D*-glucose subunits and cellulose polymers are obtained from plant material. In its native form, cellulose has a very low water solubility and thus is rather unsuitable for packaging. However, cellulose can be modified by plasticizing, surface modification or coating and blending to become water soluble, thus, modified cellulose with the addition of plasticizers provides a raw material for packaging film formation. (Hu, 2014) Recently, nanocellulose fibres have been developed from cellulose by acid hydrolysis or mechanical grinding. (Dhar et al., 2014)

Nanocellulose fibres provide high mechanical stability and optical transparency. From the fibres, with a thickness of ~15-20 nm, films and composites can be produced. (Pandey et al., 2005) The fibres from nanocellulose can be used in composites which avoids the use of inorganic fillers. (Cheng et al., 2017;

Yang et al., 2011) The incorporation of nanofibres into the polymer matrix can improve the poor moisture barrier of cellulose without affecting biodegradability. (Pandey et al., 2005)

3.1.6 Starch

Starch is a biopolymer produced by the photosynthesis of plants. Similar to cellulose, starch is composed of *D*-glucose monomers. Commercial starch is usually obtained from potatoes. Since starch crystallizes more and more over time, modifications are required to make it possible to use starch as a packaging material without any further modifications because of increasing brittleness with time. In order to use starch for industrial applications, a treatment with plasticisers is needed to improve the mechanical strength and the barrier against water. (Simon, 2011) (Doane et al., 1992)

3.2 Techniques to produce fibres for packaging material

Most synthetic and cellulosic manufactured fibres are created by “extrusion” — forcing a thick, viscous liquid through the tiny holes of a spinneret to form continuous filaments of semi-solid polymer. In their initial state, the fibre-forming polymers are solids and therefore must be first converted into a fluid state for extrusion. This is usually achieved by melting, if the polymers are thermoplastic synthetics (i.e., they soften and melt when heated), or by dissolving them in a suitable solvent if they are non-thermoplastic cellulosic (wet and dry spinning). If they cannot be dissolved or melted directly, they must be chemically treated to form soluble or thermoplastic derivatives (gel spinning). (Extrusie (textiel) - Centexbel - VKC, no date)

In this chapter, techniques to produce fibre structures from polymers are shortly outlined and schematically illustrated in **Figure 2**.

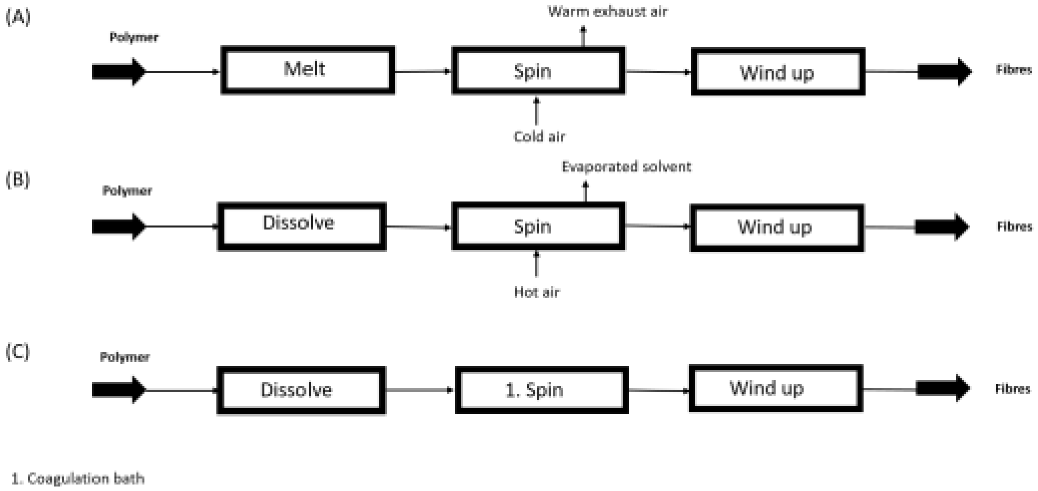


Figure 2 Spinning processes: (A) melt-spinning, (B) dry-spinning and (C) wet-spinning (illustration based on **(Bonaldi, 2018))**

3.2.1 Melt spinning

In melt spinning, the fibre-forming substance is melted before extrusion through the spinneret. The polymer is then cooled rapidly by air or water. Polyamide, polyolefins, polyester and many more polymers are produced in this manner. Melt spun fibres can be extruded from the spinneret in different cross-sectional shapes (round, trilobal, pentagonal, octagonal, and others). The extruded melt spinning technique is most frequently used for the production of fibres from biopolymers. (Bonaldi, 2018)

In the first step, the biopolymers have to be melted. The temperature depends on the melting point and the optical purity. In the second step, the molten material is extruded through the spinneret prior cooling. The fibre is then hot drawn downwards by a winding roller (**Figure 2**) that increases the strength of the fibres. (Lim et al., 2008)

Within melt spinning different settings are possible to obtain different types of yarns:

Partial oriented yarn: Mostly used for clothing textiles. These yarns are produced with a high melt draw ratio and high winding (3000-5000 m/min) but without secondary drawing.

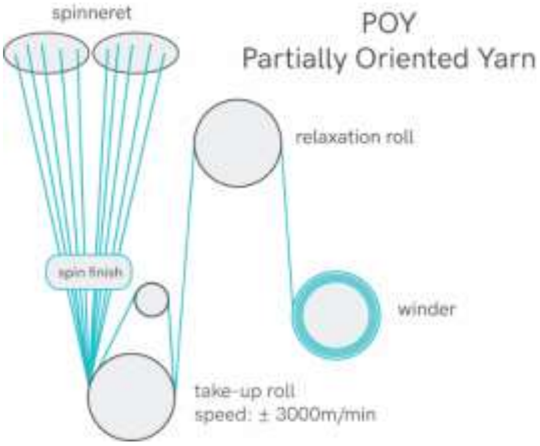


Figure 3 Partial oriented yarn (Extrusieplatform | Centexbel - VKC, no date)

Full drawn yarn: This technique is used to produce technical yarns. The yarns are produced with a low melt draw ratio followed by a secondary drawing between 2.5 and 4.

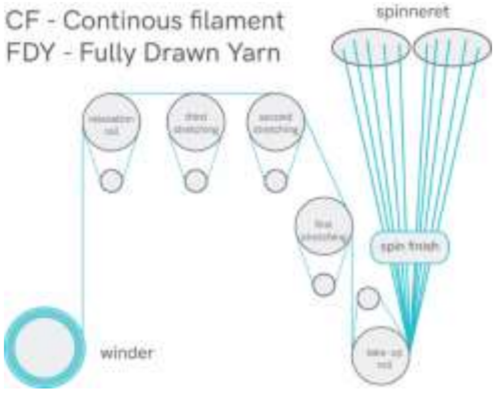


Figure 4 Continuous filament and fully drawn yarn (Extrusieplatform | Centexbel - VKC, no date)

Staple fibre: Staple fibres are produced in the same way as full drawn yarns, but the fibre bundle is cut. The cut fibre can be used for spinning or for needle felt.

Bulk continuous filament: The production is similar to fully drawn yarn but before the winder there is an air texturization in a so-called stuffer box to get a bulkier product to use in carpet products.

Monofilament: Monofilaments are thicker filaments for technical applications. They are produced at a lower production speed (200-500 m/min).

3.2.2 Dry spinning

In dry spinning processes (**Figure 2B**), the polymer is dissolved in a solvent and then extruded, as the fibres emerge through the spinneret the solvent is evaporated with hot air. This technique is used for polymers which do not melt but degrade on heating. This process may be used to produce acetate, triacetate, acrylic, modacrylic. (Bonaldi, 2018)

3.2.3 Wet spinning

The wet spinning technique (**Figure 2C**) is used for polymers that need to be dissolved in a solvent to be spun. The spinneret is submerged in a coagulation bath that causes the fibres to precipitate in the coagulation solution. Acrylic, rayon, aramid, modacrylic and spandex are produced by this process.

3.2.4 Gel spinning

Gel spinning, also known as dry-wet spinning, is used to obtain high strength or other special properties of the fibres. The polymer is in a "gel" state which means the polymer chains are partially intermingled. These interactions increase the tensile strength of the produced fibres. The polymer chains within the fibres have a large degree of orientation, which increases strength. Some high strength polyethylene and aramid fibers are produced via this process. (Introduction of Synthetic Fiber | Production Process of Different Synthetic Fibers - Textile Learner, no date)

In the EU-funded ECOBIONET project, the replacement of oil-based packaging nets with biodegradable and compostable nets was investigated. The formation from bio polyesters and PLA was improved until the desired properties such as tensile strength was present. In addition to the oriented nets, nets for shellfish products and nets in combination with plastic sheets were also investigated. All of them can be produced by extrusion melt spinning. (Industrial implementation of biodegradable and compostable packaging nets for agricultural and shellfish products, no date)

Through adapting and fine-tuning of the extrusion process, the properties of the yarn can be adjusted such as the mechanical properties. The processing parameters that can be adapted are the following: extruder and die temperature, throughput, drawing rollers speed and temperature, die geometry, shear rate, melt and cold draw ratio, spin finish application, etc. The success of the extrusion process itself can be determined via filament homogeneity, production speed, maximum drawing rate, filament breakage and observation of any anomalies.

4 Packaging material - Bio-based polyester

At the present time, considerable efforts are being made to achieve the commercialisation of novel biopolymers with improved properties and new functionalities in packaging, textile, and other applications. These innovations are driven by the increasing demand for sustainable products by consumers and brands alike due to the growing awareness of the impact on the environment and the need to reduce the dependency of fossil resources.

Of special interest are the fully bio-based aromatic polyester polyethylene furanoate (PEF) and the varied and large group of polyhydroxyalkanoates (PHAs), natural polyesters that are biodegradable in numerous environments.

4.1 Polyethylene furanoate (PEF)

As already introduced for new textile materials (**section 3.1.4**), PEF is currently under development also as alternative plastic packaging material. PEF is a 100% bio-based polyester that is polymerised from 2,5-furandicarboxylic acid (FDCA) and monoethylene glycol (MEG) through polycondensation (**Figure 5**). FDCA is a monomer derived from sugars using biofermentation, which can replace oil-based terephthalic acid (TA) in polyethylene terephthalate PET to make PEF.

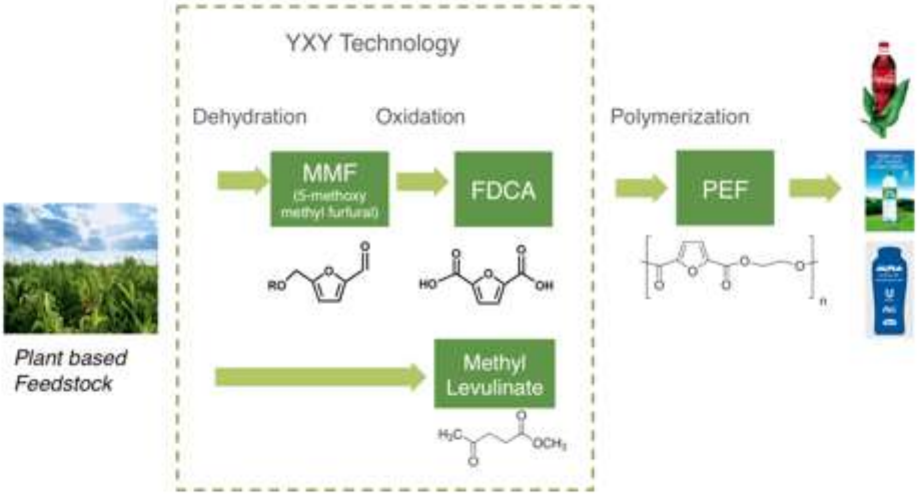


Figure 5 YXY Technology used to create PEF (illustration with permission of Avantium)

In order to produce PEF, first generation bio-feedstock – such as corn- or wheat-based sugars – can be used. Second generation feedstock such as waste, wood, wheat-straw, corn sotver or bagasse, could also be considered when it becomes economically viable. (Eerhart, A. J. J. E. et al., 2012)

PEF presents interesting barrier and thermal properties compared to PET:

- 10 times better barrier to oxygen (Burgess et al., 2014)
- 10 times better barrier to carbon dioxide (Burgess et al., 2015)
- Twice as good water vapour barrier (Avantium, no date a)
- Glass transition temperature of PEF is 87°C compared to the glass transition temperature of PET at 79°C (Konstantopoulou et al., 2017)

- Melting temperature of PEF is at about 220 °C compared 255°C of PET (Konstantopoulou et al., 2017)

Due to these properties, PEF is a very convenient material to be used in packaging, specifically in beverage bottles, trays, cup films and laminates. Other applications include textile fibres and multiple film types, such as pouches, wrappers and shrink film. (Kemeling and van Berkel, 2015) The barrier properties of PEF lead to an extended product shelf life, which contributes to reduce food and beverage waste during transport and storage. According to the European Food Safety Authority, this material is suitable for food contact. (Scientific Opinion on the safety assessment of the substance, furan-2, 5-dicarboxylic acid, CAS No 3238-40-2, for use in food contact materials}, 2018) Furthermore, PEF's higher mechanical strength compared to PET enables more design options, better shaping of bottles and the development of thinner walls while maintaining the integrity of the bottle during top-load and handling. (Kemeling and van Berkel, 2015) In conclusion, the enhanced barrier and mechanical properties of PEF compared to PET facilitate the production of lighter bottles as well as smaller bottles with a higher surface to volume ratio without having a negative impact on the shelf life. (Kemeling and van Berkel, 2015)

Figure 6 Bottle made from PEF (Avantium)

The chemical resemblance of PEF and PET allows similar production steps and quality control methods. Furthermore, processing can be done on machines designed for PET with the implementation of minor changes in conditions or equipment. The processing of PEF consists of an injection or extrusion process followed by an orientation process to create the strain induced crystallization. This can optionally be followed by a heat step. The lower melting point of PEF typically allows lower processing temperatures than PET, which can lead to lower energy costs. (Kemeling and van Berkel, 2015) PEF is suitable for mechanical recycling. The PEF producer Synvina has obtained interim approval from the European PET Bottle Platform for the recyclability of its PEF bottles in the European Union (from its intended 50,000 tons reference plant).

PEF is predicted to enter commercial scale in 2023, this material is expected to reach a share of approximately 2.7% (70,000 tonnes) of the global production capacities of bioplastics in the next five years (**Figure 7**). (European Bioplastics and Nova-Institute (2018))

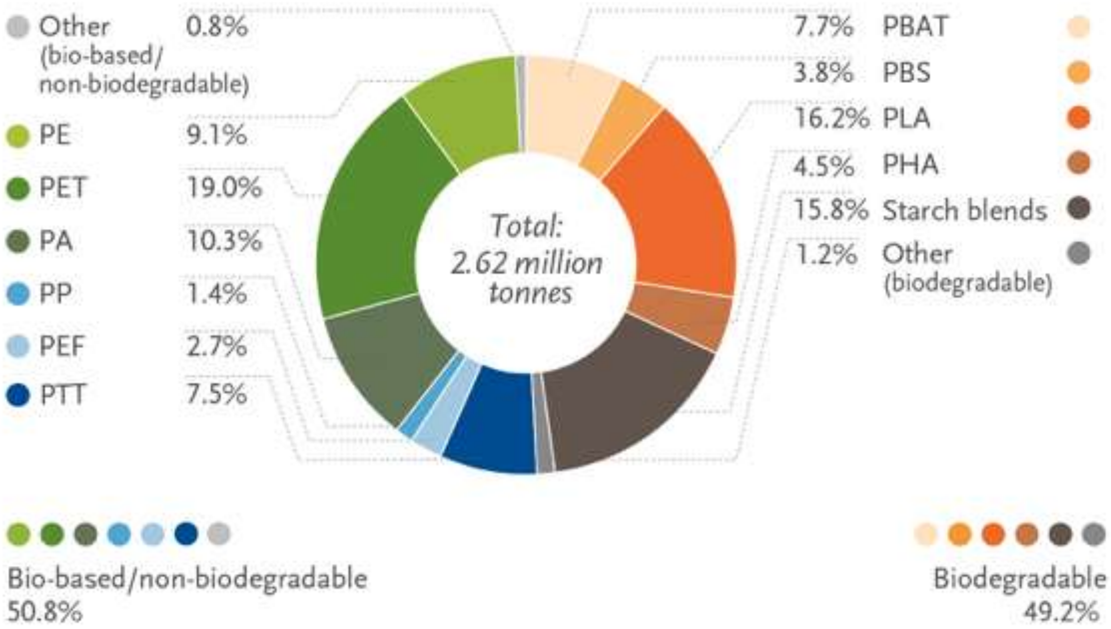


Figure 7 Expected global production capacities of bioplastics by 2023 sorted by material type (European Bioplastics, Nova-Institute, 2018, with permission from EUBP)

4.2 Polyhydroxyalkanoate (PHA)

PHAs are an important polymer family with very interesting properties that see a strong interest and numerous activities by researchers but are also available at commercial scale. These polyesters are 100% bio-based and biodegradable and feature a wide array of physical and mechanical properties depending on their chemical composition. PHAs are produced by microbial fermentation of sugars using a variety of microorganisms. PHAs can be used pure, blended, or as an additive to modify other polymers such as polylactic acid. In order to obtain bioplastics made from PHAs, the biopolymer has to be removed from the bacterial cell material, cleaned and compounded. (Thielen, 2012)

The chemical composition of PHAs can be modified depending on the combinations of monomer subunits. PHAs are produced either as homopolymers or copolymers. Homopolymers are made of one type of PHA throughout the entire structure – such as pure poly(3-hydroxybutyrate) (P3HB) or poly(4-hydroxybutyrate) (P4HB). Copolymers, on the other hand, consist of two or more different PHAs throughout the structure of the polymer chain. Most common industrially produced PHAs are limited to using P3HB and one other PHA as the co-monomer. (Cambridge Consultants, no date)

PHA polymer properties include:

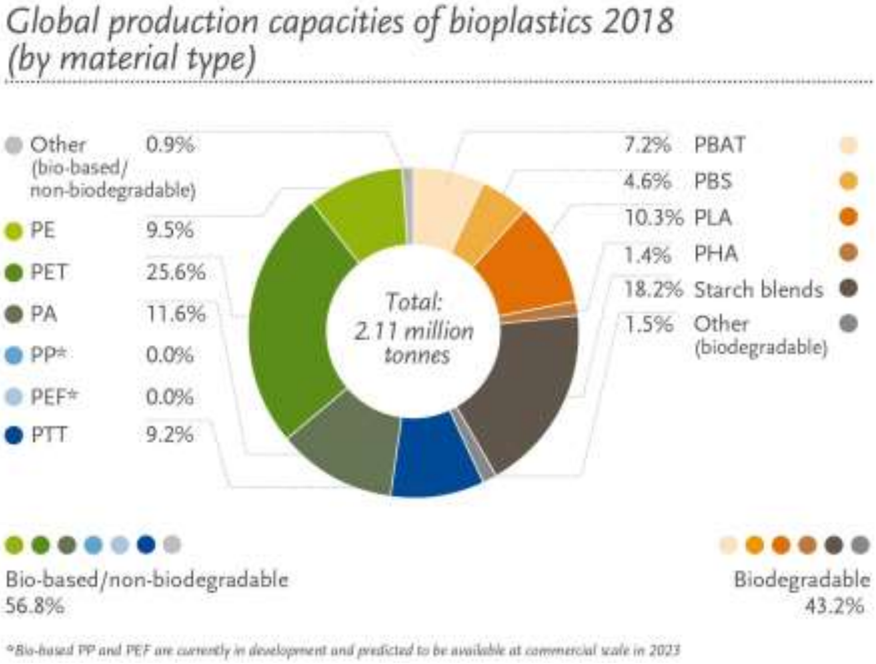
- Good heat and ultraviolet light resistance (Pepsico, 2019)
- Approval for food contact by the US Food and Drugs Administration (FDA) (Pepsico, 2019)
- Suitable for food preservation (Pepsico, 2019)
- Can be formulated for different purposes (Pepsico, 2019)
- Durable for high speed processing (Pepsico, 2019)
- Able to withstand high temperatures while in storage (Pepsico, 2019)Capable of binding with other materials (e.g. paper) (Pepsico, 2019)

Due to these interesting properties and their versatility, PHAs can be used in a wide range of applications, for instance, for packing potato crisps (**Figure 8**). Some degree of market penetration has already been achieved in the production of packaging, coatings and hygiene products. It is foreseen that PHAs enter further market segments, such as environmental services, automotive, electronics, fishing and fuels. (Cambridge Consultants, no date)

Figure 8 Industrial compostable bag made of PHA developed by Danimer Scientific and PepsiCo (Pepsico, 2019)

PHAs can be designed for different end-of-life solutions: These can be either composted in an industrial composting plant or biogas installation, as well as on a home compost heap. Furthermore, some PHAs can biodegrade in different environments (e.g. soil or marine environment). (Thielen, 2012)

Currently, PHA represents 1.4% (29,000 tonnes) of the global production capacities of bioplastics in 2018 (**Figure 9**). The market presence of PHAs is still limited compared to other materials mainly due to the price level (5€/kg for a density of 1,200 – 1,250 kg/m3). However, different ways are being explored to lower the price of PHA, including using waste as a feedstock or up-scaling of biotechnological production (van den Oever et al., 2017). By 2023, it is foreseen that PHA will reach a share of 4.5% (117,000 tonnes) (**Figure 7.**) (European Bioplastics, 2019a)



*Bio-based PP and PEF are currently in development and predicted to be available at commercial scale in 2023

Figure 9 Global production capacities of bioplastics 2018 by material type (with permission from EUBP)

5 Developments of copolymers and compounds with tailored biodegradability

5.1 Lactic Acid mono- and co-polymers: synthesis and characteristics

Among the biodegradable polymers, PLA-based polymers are one of the most extensively studied synthetic polymers from biomass. They are used for a wide range of applications covering disposable household items, food packaging, agricultural films, drug delivery systems, and implantable biomedical devices. However, some PLA properties are still insufficient as it presents issues such as low toughness and impact resistance. Moreover, its degradation rate cannot meet the needs of many applications. (Cheng et al., 2009; Mehta et al., 2005)

5.1.1 Synthesis of PLA

Polylactic acid is an aliphatic polyester that can be synthesized by lactic acid or by lactide (**Figure 11**). Lactic acid, or 2-hydroxypropanoic acid, present hydroxyl and carboxylic acid functionalization that can lead to intermolecular esterification reactions. Self-esterification of lactic acid at 120-135 ºC leads to formation of the cyclic dimer lactide, or 6-dimethyl-1,4-dioxane-2,5-dione, which is insoluble in water. (Auras et al., 2010)

These two monomers present respectively one and two stereo centres and thus are present in nature in the two enantiomeric forms (*L*- or *D*) or, in the case of lactide, *R,R/S,S/R,S* diastereoisomers.

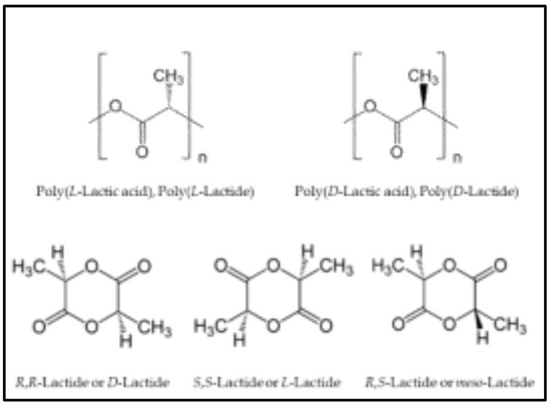


Figure 10 PLA monomers. (redrawn)

Polylactic acid obtains a mouldable stereochemical structure that may be easily modified by controlling the ratio of its *L*- or *D*- isomers during the polymerization. Indeed, generally PLA is a copolymer constituted by poly(*L*-lactic acid) (PLLA), which confers crystallinity to the structure, and poly(*D,L*-lactic acid) (PDLLA), which leads to amorphous polymers (**Figure 11**). (Auras et al., 2010)

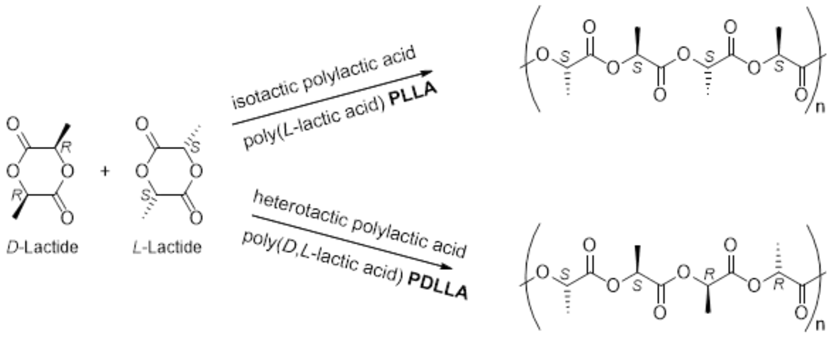


Figure 11 Possible tacticities of polylactic acid. (redrawn)

Moreover, it is known that the content of R-enantiomer affects the glass transition of PLA, which decreases with increasing R to S enantiomer ratio. Thus, many properties of PLA can be controlled by the ratio between the enantiomers and, to lesser extent, by the catalytic system used. (Auras et al., 2010) Generally, commercial grade of PLA are co-polymers of *L*-lactic acid and *D*-lactic acid or the corresponding lactide forms. (NatureWorks, no date) In industrial packaging applications, the use of PLA with a content of *D* units of a 2–6 wt. % randomly distributed is very common, with this formulation the crystallization of PLA is low, favouring the production of amorphous transparent films (in contrast to textiles which need high crystallinity).

The synthesis of PLA can be divided in two techniques based on the monomer used for the polymerization: (Auras et al., 2010; Garlotta, 2001)

Direct polycondensation (DP): DP of lactic acid is usually performed in bulk by distillation of condensation water with or without a catalyst, while vacuum and temperature are progressively increased. A polymer of low molecular weight and uncontrolled stereoregularity is obtained, this result is the main disadvantage of DP and restricts its use. The polymer thus possesses inferior mechanical properties. So, this method is normally employed only to obtain polymers of low molecular weight.

Ring-opening polymerization (ROP): While DP of lactic acid is cheap and easy, the end product can hardly be controlled. For commercial production of PLA usually the ROP technique is used. ROP is the method used for lactide polymerization via a catalysed coordination-insertion mechanism. (Li et al., 2008) ROP is the most preferred route to produce high molecular weight PLA on industrial scale. The selection of monomer enantiomer ratio and of catalyst is of main importance in ROP due to the different properties that may be conferred to the final product, thus controlling its physico-chemical, mechanical properties and biodegradability. ROP of *L*-lactide is generally the most preferred reaction route, while alkoxides of Sn, in particular stannous 2-ethylhexanoate (tin octanoate), are the most common catalysts used for low crystalline PLA. Semicrystalline PLAs have been produced from both meso-lactide (yielding syndiotactic PLA) and racemic lactide (yielding stereoblock isotactic PLA) using chiral aluminium catalysts containing bulky ligands. (Ovitt and Coates, 2000); (Radano et al., 2000)

Thanks to the high control of the chemistry and stereochemistry in the reaction, which lead to the possibility to modulate the characteristics of the final product. ROP have been successfully carried out by melt, solution, bulk and suspension techniques, each of these methods has its own advantages and disadvantages, but melt polymerization is generally considered the most simple and reproducible technique. (Auras et al., 2010) ROP has been subject of several investigations and led to several patents, mainly not involving PLA co-polymers and thus exceeding the purpose of this work. (Enomoto et al., 1994; Grubber et al., 1992; Maeda et al., 1999) Nevertheless, investigation on the topic is still in progress, as an example, NatureWorks LLC, partner of the project on which this review is founded, has developed a solvent-free, low-cost continuous process for the production of PLA from corn-derived dextrose. The resulting commercial PLA (Ingeo™) is the first synthetic polymer to be produced from renewable resources. Metal complexes, organic compounds or enzymes to yield high molecular weight PLA in excellent composition and purity can initiate the ROP of lactide.

Reactive Extrusion (REX): REX of PLA is a new specialty in ROP reactions that has recently emerged in small scale investigations as a tool with the potential to replace chemical batch reactor. REX, performed in a well-designed twin-screw co-rotating extruder (**chapter 5.2**), is an attractive route for bioplastic processing in order to carry out homo- or co-polymerizations. The obvious advantages of an extrusion polymerization are that it is a solvent free and low-cost continuous process, starting from monomers or pre-polymers and resulting in polymers, while controlling the chemistry throughout the process. (Raquez et al., 2014) Recently, a one-step REX method was filed as patent to produce a biodegradable composite composed of a polymeric matrix and one more other constituents (WO2019113713A1)

5.1.2 Biodegradation of PLA

Several studies in the literature suggest relationships between the chemical structure of substrates and their degradation rates. Likewise, the polymers exhibiting the lowest mechanical properties are also generally the ones with the highest degradation rates. This issue is the reason for the limited feasibility of commercially available home compostable shopping bags. High biodegradability rates depend primarily on (1) the presence of terminal hydroxyl or acyl functional groups to allow for metabolic processes and (2) low molecular weights. Such findings suggest that in many cases biodegradability may be directed by physico-chemical phenomena, such as the mobility of substrate, availability, mixing, mechanical properties affecting the breakdown of the macrostructure, and/or hydrophilicity of chemical species. Bio-based or bio-renewable monomers can lead to materials that are only partly biodegradable. Unfortunately, biodegradability of a large number of novel bio-based systems has not been investigated yet. Changes in the functional groups of bio-based monomers, crosslink density and co-polymerization with non-biodegradable comonomers can lead to materials having various degrees of biodegradability. Overall, biodegradability highly depends on the environmental conditions.

The biodegradation of plastics is a complex process involving multiple steps and pathways and is highly dependent on the conditions. Characteristics of the polymer influencing the biodegradation are the degree of crystallinity of the polymer, the chemical structure, the solid-state morphology as well as the hydrophilicity-hydrophobicity ratio. If the crystallinity is low, the diffusion of water vapour (as well as other gases) in the material is facilitated resulting in an improved hydrolytic efficiency and thus biodegradability. As the crystallinity depends on the structural order of the chain, a higher crystallinity degree can be reached in PLLA, but not in PLA containing a significant amount of D-lactic acid. Besides crystallinity of PLA, the polarity, and thus the hydrophilicity, as water is a very polar molecule, also affects biodegradation. This is because hydrophilic materials undergo hydrolysis more easily, thus biodegradation is enhanced. Moreover, a low molecular weight PLA can more easily be degraded by microorganisms. Following the last considerations, a low molecular weight, much irregular and more hydrophilic PLA could be a good option to improve biodegradation. However, a low molecular weight is generally detrimental for processing and mechanical properties, whereas an improved polarity can be detrimental for barrier properties towards water (¡Error! No se encuentra el origen de la referencia.). Hence, for achieving the desired properties generally compromises are necessary. Alternatively, copolymers can be added to adjust the properties of PLA as outlined in (**chapter 5.1.2**).

Biodegradation process involves three steps, first a depolymerization process leading to the formation of PLA oligomers, second the oligomers need to be further cleaved in lactic acid units that third are consumed in the citric acid cycle where they are converted into carbon dioxide and water by enzymes produced by microorganisms, while a portion of the carbon is converted into biomass. (Maharana et al., 2009; Mueller, 2006; Stloukal et al., 2015)

The initial degradation step for PLA occurs preferentially in amorphous regions, where the ester groups are hydrolytically degraded in the presence of water. Thus, the number of oligomers after chain scission will depend upon the number of ester bonds present in the PLA main chain. (Maharana et al., 2009) The carboxylic end groups act catalytically to affect the hydrolytic degradation of PLA in a self-catalysed and self-maintaining process, where the degradation rate is faster for low-molecular-weight, more hydrophilic and more amorphous chains, thus the initial degradation into smaller fragments is the rate limiting step in biodegradation processes. (Elsawy et al., 2017; Husárová et al., 2014; Lyu et al., 2007) PLA becomes water-soluble when the molecular weight is below 20,000 g/mol and can be uptaken by microorganisms, undergoing the metabolic process converting it into carbon dioxide, water and biomass. (Gorrasi and Pantani, 2013; Kijchavengkul et al., 2008; Mueller, 2006)

A study by Tsuji et al., 2019 showed that in a process not involving enzymatic degradation, the position in the polymer chain of the ester group (end or central group) does not affect the hydrolytic degradability of PLA-based materials, as long as the polymers are composed of one monomer unit. (Auras et al., 2010) The composting process of PLA proceeds efficiently under adequate conditions due to the combined effects of hydrolysis and microbial activity. (Ghorpade et al., 2001) Recently, a patent declares a protease variant that is especially suitable for PLA degradation. (WO2019122308A1) Besides microorganisms and enzymes needed for degradation, the elevated temperatures encountered during composting is important and may accelerate the hydrolysis process of PLA, especially when temperatures exceed 50ºC. (Tokiwa and Jarerat, 2004) Moreover, it is reported that the cleavage of PLA chains can be enhanced by use of extracellular enzymes released by specific microorganisms, which contribute to the degradation processes. (Garrison et al., 2016)

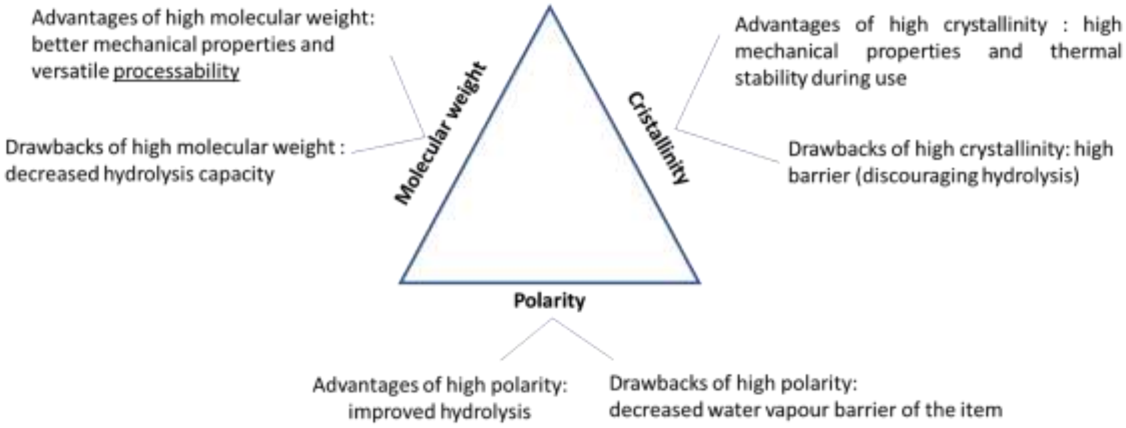


Figure 12 Overview of influencing biodegradation of PLA.

5.1.3 Copolymers of PLA

As reported above, the crystallinity of PLA (Elsawy et al., 2017) as well as its hydrophilicity influence the biodegradation process. (Maharana et al., 2009) The introduction of different monomers (dicarboxylic acids) in the PLA chain reduces PLA crystallization. Thus, copolymers can be used to tailor besides crystallinity and hydrophilicity also molecular mass, flexibility and orientation of the backbone chains. While the presence of a methylene group in position alpha to the carboxylic acid of LA hinders its biodegradation, the selection of polymers without this steric hindrance favours biodegradability because microorganism can access the carbonyl group easier. The choice of initiator system, co-initiator as chain control agent, catalyst concentration, monomer-to-initiator ratio and polymerization temperature and time, significantly affects the polymer properties, such as the molecular weight, degree of crystallinity, and residual monomer content, which in turn affect the physico-mechanical properties and processing temperature range of the polylactide and its copolymers as well as their biodegradation behaviour.

To date, there is a lot of research going on on copolymerization of lactide molecules. For instance, glycolic acid is the most studied co-monomer used with lactic acid. (Blasi, 2019; Perinelli et al., 2019; Sharma et al., 2019) A recent example is reported by Tsuji et al., 2019 who investigated the controlled enantiomeric alternating co-polymerization of L- and D- lactides with glycolic acid and their stereocomplexation in terms of crystallinity and physical properties. (Tsuji et al., 2019) Moreover, block co-polymerization of PLA with poly(ethylene glycol) (PEG) is another common technique to enhance biodegradability of polylactide. (Koosomsuan et al., 2019; Liu et al., 2019; Perinelli et al., 2019; Sharma et al., 2019) Zhang et al., 2019 recently investigated the synthesis of a norbornene-functionalized lactide copolymerized by grafting with polyethylene glycol monomethyl ether and isopropylamide reporting an enhanced biodegradation and the possibility to control phase transition temperatures of the final product. (Zhang et al., 2019) An interesting study revealed a solvent-free synthesis of a PLA-PEG block copolymer that enhanced biodegradability. (Lee et al., 2019)

Copolymers of PLA with GA or PEG are known for medicine applications and drug delivery systems, but also terpolymers of the three are known. For example, poly(lactic-co-glycolic acid)-poly(ethylene glycol)-poly(lactic-co-glycolic acid) (PLGA–PEG–PLGA) was developed to give enhanced pseudoplastic characteristic to self-hardening tricalcium phosphate cement for bone regeneration application. (Vojtova et al., 2019)

Another possibility to tailor crystallinity and degradability of PLA is the synthesis of a star-shaped polymer due to the use of xylitol as copolymer. (Dasgupta et al., 2019) This alcohol with five functionalities has been used for the synthesis of a 5-arm star-shaped PLA, which is reported to be completely amorphous and obtaining faster hydrolytic degradation rates already with addition of 2% xylitol. (Teng et al., 2015)

Copolymerization of lactide with lactone-type monomers have also been studied, the most used comonomers of this family are β-butyrolactone, δ-valerolactone and ε-caprolactone. Navarro et al., 2019 recently drafted a patent for the synthesis of a biodegradable nanostructured block copolymer composed of PLA and β-butyrolactone. Shi et al., 2019 investigated the crystallization behaviour of different polylactide/poly(δ-valerolactone) supramolecular copolymers in the presence of 2-ureido-4-[1H]-pyrimidinone, reporting the possibility to tailor the degree of crystallization by introducing stereocomplexation.

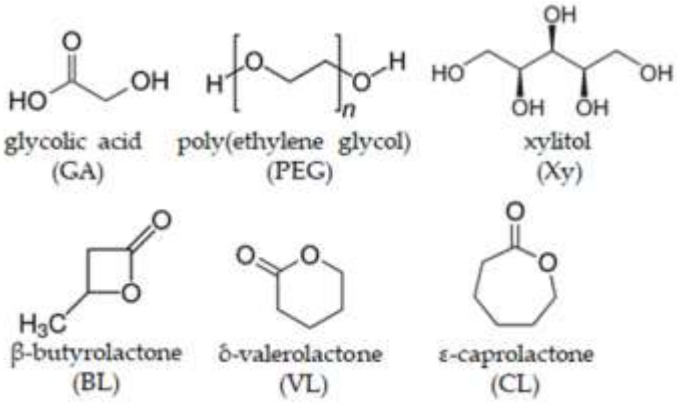


Figure 13 Structure of various monomers (redrawn)

As reported before, carboxylic groups formed during the first steps of the biodegradation act as catalysts for further steps of the degradation. (Elsawy et al., 2017) The presence of anhydrides in the polymer chain lead to the formation of two carboxylic groups in the degradation process. Storey and Taylor, 1997 have successfully demonstrated that the presence of the anhydride linkages allowing a relatively rapid decrease in molecular weight, the extent of which is governed by the concentration of the anhydride linkages along the chain, followed by a slower degradation of the remaining oligomer the rate of which is governed by the composition of original polyester prepolymers. (Storey and Taylor, 1997) Various types of polyanhydrides, such as aliphatic or aromatic polyanhydrides, poly(ester-anhydride), poly(ether anhydride), and poly(amide anhydride) have emerged for use in various applications. The poly(ester-anhydride)s have extended advantages as compared with another polymer alone because they show the properties of both bulk degradation and surface erosion, which are shown by polyesters and polyanhydrides, respectively. (Soni et al., 2019) Pfeifer et al., 2005 successfully synthesized poly(ether anhydride) micro- and nanospheres by copolymerization of sebacic and lactic acids which showed enhanced degradation compared to the respective homopolymers. (Pfeifer et al., 2005)

Considering that PLA is a polymer that can be obtained by biomass resources, (Paula et al., 2018; Singhvi and Gokhale, 2013) different poly(ester-anhydride)s have been developed with different diacid comonomers in order to maintain this aspect while tailoring enhanced biodegradability characteristics. In 2004, U.S. department of energy individuated 12 strategic building block chemicals derived from carbohydrates that can be produced by biological or chemical conversion from biomasses. (Werpy and Petersen, 2004) Most of these building blocks are bifunctional dicarboxylic acids such as malic acid, succinic acid or itaconic acid, that are suitable candidates for copolymerization with lactide to obtain biodegradable copolymers. Dicarboxylic acids such as malic acid or succinic acid are inexpensive and non-toxic chemicals that are naturally present in vegetables and fruits, where they are synthesized during the fermentation process by microorganisms. (Thessrimuang and Prachayawarakorn, 2019)

5.1.3.1 Malic acid

Companies such as Novozymes and Myriant have developed proprietary technologies based on aforementioned fermentation process. Currently, 80% of global malic acid is produced synthetically and the remaining is produced by renewable sources among other from fruit waste. Commercialization of bio-based malic acid at competitive pricing as compared to its synthetic counterpart is expected to create immense opportunities to be used as platform chemical in the future. The estimated price of bio-based MA is around 2400 €/tonne. At the market price of 1.9 €/kg, MA production from soy molasses via PMA fermentation offers an economically competitive process. MA is used to produce bio-based polyesters which find application in pharmaceuticals used to treat cancer cells. It has been demonstrated that poly(malic acid-co-*L*-lactide) acts as a superb degradation accelerator for PLA in physiological conditions due to the superiority of poly(malic acid) vs. PLA to biodegrade. Their findings also proved the usefulness to tune the degradation rate.

Nowadays, many researchers are interested in the production of microbial malic acid due to the estimated industrial demand, microbial production of malic acid is effective and eco-friendly. (Cheng et al., 2017; Iyyappan et al., 2019)

Gazzotti et al., 2019 recently reported an innovative study about the synthesis of a PLA functionalized polymers starting from a derivative of malic acid O-carboxyanhydrate monomers, presenting a new alternative for the preparation of PLA-based materials. Poly(malic acid-co-*L*-lactide) acts as a strong degradation accelerator for PLA under physiological conditions. Klicken oder tippen Sie hier, um Text einzugeben. (Oyama et al., 2016; Zhang et al., 2015)

5.1.3.2 Succinic acid

Nowadays, the bulk of SA is produced at a rate of 25,000 tons per year from maleic anhydride obtained by oxidation of the C4 fraction (n-butane or butadiene) of crude oil. However, the biotechnological production of SA by fermentation of carbohydrates has attracted recent attention. At larger scale (typically 50 kTons), and due to lower costs of raw materials, bio-SA has the potential to be cheaper than its fossil-derived product and is expected to open up new markets and applications. Reverdia (currently Roquette) and Myriant's production cost for bio-SA is estimated to be lower than 1,040€/MT whereas market prices for petroleum-derived SA are reported between $6,000 and $9,000/MT. Building on such advantage, the most conservative market studies estimate 250 ktons of bio-based SA will be produced by 2020 with high opportunities for growth in the EU. Some of the major companies dominating this market are Reverdia/Roquette, BioAmber and Succinity. As an example of copolymerization, LA, ethylene glycol and SA were copolymerised by direct polycondensation. The lack of methyl groups in the succinic molecule favoured the biodegradation of its derivatives such as poly(butylene succinate) (PBS). In fact, PBS is home compostable according to Vinçotte certificate. For that reason, it is an interesting blend partner for PLA. However, most PBS on the market is not yet bio-based and its market is less established than that of PLA. Possibility of terpolymers with adipic acid are interesting solutions to be addressed too.

Even if succinic acid is actually produced as derivative of maleic anhydride, biotechnological production of succinic acid by fermentation of carbohydrates has attracted recent attention. The industrial-scale production of succinic acid is reported to be viable by fermentation with bacteria, fungi or yeast. Moreover, it is reported that renewable raw materials such as industrial waste and by-product streams may be used as resources for succinic acid production. (Ferone et al., 2019) Even if succinic acid is more commonly used in PLA blends when co-polymerized to 1,4 butanediol-co-polybutylene succinate (Ding et al., 2019; Su et al., 2019), there are also studies about their direct copolymerization. As example, Cadar et al., 2012 investigated the biodegradation behaviour of poly(lactic acid-co-ethylene-co-succinic acid) copolymers. The lack of methyl groups in the succinic molecule, compared to the lactic acid, is reported to favour the biodegradation and the decomposition behaviour of its derivatives such as poly(butylene succinate) are well demonstrated. (Cadar et al., 2012)

5.1.3.3 Itaconic acid

Finally, itaconic acid, or methylene succinic acid, is a diacid produced on an industrial scale via bio-based fermentation with *Aspergillus terreus*. Itaconic acid has been intensively studied as an alternative co-monomer for acrylic acid and methacrylic acid. (Robert and Friebel, 2016) As example, Sood et al., 2017 and Gupta et al., 2018 reported the synthesis of a biodegradable hydrogel of poly-(lactic acid-co-itaconic acid) copolymerized by microwave assisted technique for drug delivery purposes. (Gupta et al., 2018; Sood et al., 2017)

As seen, polymer biodegradability depends on polymer crystallinity, crosslinking and molecular weight. In addition, the selection of proper additives, in particular plasticizers and fillers can speed up the biodegradation of polymer based materials. (Chiellini et al., 2004; Corti et al., 2002) Plasticizers lower the glass transition temperature of polymers and promote the rubber state that is easier to biodegrade, as experienced by INSTM and OWS on cellulose di-acetate blends plasticized with triacetin (Phuong, Verstichel et al., 2014), a GRAS compound according to FDA. In PLA-based blends (Bugnicourt et al., 2014b) the selection of proper plasticizer type and amount allows promoting the biodegradability. In order to avoid migration of excessive plasticizers with consequent changes in mechanical properties during ageing and possible contamination in case of packed items, the use of reactive plasticizers and their reaction with the polymeric matrix, possibly in the extrusion step, is an interesting approach. As such, reactive extrusion will be also used in the preparation of blends besides the copolymerisation step. It has been proven by INSTM that epoxy functionalised plasticizers are bio-based and for food contact approved. Thus, epoxydised agro-based derivates plasticizers can be used for the production of PLA based transparent films (Lazzeri et al., 2013) bio-based. Further bio-based plasticizers are acetyl tributyl citrate and functionalised (epoxy, maleic) oligomers of LA as well as epoxy derived natural oils such as soybean oil derivates. INSTM has also already experienced positively the use of LA oligomers as plasticizers in PLA achieving valuable mechanical properties and biodegradability. The effect of nucleating agents such as PDLA (Aliotta et al., 2017), talc, calcium carbonate or even montmorillonites (Castiello et al., 2012; Scatto et al., 2013), etc. are currently studied in order to modulate the biodegradation properties of PLA Such inorganic fillers in small amounts also improve processing of PLA blends avoiding sticking on the mould or of blow moulded films.

Overall, home compostable polymers like PCL or PBS for packaging material are limited due to low properties especially low mechanical properties and high costs. Thus, PLA seems the most promising polymer for bio-based packaging application so far. To enhance biodegradability of PLA, the use of enzymes mixed with polymers is under research. However, the BIOCLEAN project (New Biotechnological approaches for biodegrading and promoting the environmental biotransformation of synthetic polymeric materials, no date) among other studies (Publications | OWS}, no date) concluded that none of the tested enzymes showed degradation capability towards tested conventional polymers. In the case of PLA, Carbios, a French company, has developed a pilot technology for embedding an enzyme in plastic at the time of production. (Carbios | Reinvent Polymers Lifecycle, no date)

5.1.4 Biocomposites with natural fillers fraction from agro-industrial waste

Likewise, biocomposites using natural fibres or fillers have been researched intensively over the last years yielding to new applications due to their processing advantages, biodegradability, low cost, low relative density, high specific strength and renewable nature. Several examples of biodegradable composites are reported in literature using different types of matrixes, e.g. starch based blends and PLA, and natural reinforcements such as fillers from pine, cellulose, potato pulp, rice husk (I Wayan et al., 2014). Natural filler considerably reduces the price of the final material since generally natural fillers are cheaper than bio-based polymeric matrices such as PLA. Moreover, if proper compatibility is achieved, fillers can strengthen the material and increase the Young's modulus or impact resistance. Besides, composites can promote biodegradability, as the presence of fillers increase the polymer surface available for microbial attack especially when the fillers are based on easily degradable natural components (Seggiani et al., 2015), such as cellulose or by-products with high content in hemicellulose. The swelling and degradation of the fillers highly promote the disintegration of composite material (Green, 2012). The amount of fillers loaded in a composite is limited by weak adhesion at the fibre-polymeric matrix interphase, poor mechanical properties and difficulties in processing. (Chiellini et al., 2001; 2004) Therefore, the use of compatibilizers such as maleic or itaconic anhydride may allow to obtain a higher load of fillers in PLA polymeric matrix. As well as fillers pre-treatment, the amount and properties of the coupling agent are also crucial for the properties of the composites (Seggiani et al., 2015).

5.2 Upscaling and industrial processing of copolymers

Extruders are generally classified into a single-screw and a twin-screw type: The single-screw extruder is applied to general polymer processing (blow moulding, film making and injection moulding), while a twin-screw extruder is mainly used for compounding and polymer blending. In fact, the two type of extruders have significant differences: in a single-screw the friction between the materials, the rotating screw, and the barrel allows the material to rotate and push forward, which generates heat. Although it realizes a good quality melt, it generates high pressure, which compresses the dispersed particulates leading to agglomeration and poor mixing due to insufficient shear deformation. In contrast, the twin-screw extrusion heating is independent as the intermeshing screws push the material forward with the relative motion of the flight of one screw inside the channel on the other. Therefore, depending on the level of shear and the speed of the screw, the twin screws can orient polymer melt in varying configurations. (Gigante, 2019) Most of the production of polymer blends is done in twin-screw extruders.

A summary of main peculiarities of the two systems is represented in the following table (**Table 5.1**).

Table 5.1 Qualitative differences between single-screw and twin-screw extrusion (adapted by (Sakai, 2013))

Twin-Screw	Single-Screw
Good feeding	Fair feeding
Starve feeding	Flood feeding
Good melting	Fair melting
Good distributive and dispersive mixing	Fair mixing (disruptive mixing)
Self-wiping	Nonself wiping
Modular design (flexible)	Non-modular design
Good degassing	Fair degassing
Limited pressurization	Good pressurization

Following the increase in plastics production, the demand for larger extrusion capacity and better mixing performance drastically increased and therefore a twin-screw extruder played a more important role in capacity increase than a single-screw extruder in the field of compounding/pelletizing since early 1970s. (Gigante, 2019) Some mixing elements in the screws can be applied to obtain different operational purposes with wide variety of materials. Furthermore, studies on polymeric melt (Dhanasekharan and Kokini, 2003; Shah and Gupta, 2004) stated that between co-rotating and counter-rotating twin-screw extruder, the former is more suitable for applications such as compounding, mixing and chemical reaction, because of the complexity of the flow in the intermeshing region, which provides them good mixing and compounding characteristics. The phase morphology conformation of the polymer blends depends on the processing conditions (such as temperature, pressure, shear rate, residence time and feeding sequence) and the material properties (molecular structure, melt viscosity, melt elasticity and surface tension). (Gigante, 2019) One important aspect of biopolymer processing is to control humidity: High humidity during polymer extrusion increases melt fluidity due to chain scission, hence, industrial plants must be equipped with proper drying sections. In this equipment, usually pellets of biopolyesters are heated in presence of a dried air flow, with a low dew point, maintaining them stirred to avoid undesired agglomeration, before extrusion. (Coltelli et al., 2018)

5.2.1 Processing for production of flexible packaging

In general, the production of flexible packaging is based on the preparation of plastic films, using different converting processes, such as for example extrusion flat die extrusion (**Figure 14**) and blown film (**Figure 15**).

Flat die extrusion (**Figure 14**) allows the production of polymeric sheets and films (with a thickness ranging between 50 microns and one millimetre) and consists of the extrusion of the molten polymer through a linear die of rectangular geometry. The material comes out from the die in the form of a molten plate that is immediately in contact with a thermostatic roller to allow cooling and solidification. Due to the motion of the roller, the film undergoes elongation with a consequent reduction in thickness. The film then passes through a second roller and to a measuring, cutting and winding station (**Figure 14**). The operating parameters to be controlled during flat die extrusion are the extrusion and windup rolls temperatures, distance between die and the first roll and the draw ratio (ratio between windup roll speed and polymer speed at the die exit): all of these have a big influence on the final product characteristics (morphologically and mechanically). (Coltelli et al., 2018)

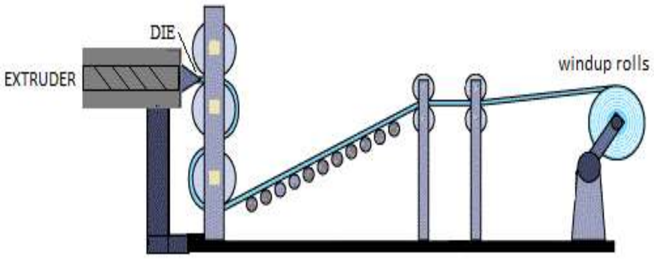


Figure 14 Schematic diagram of the flat die extrusion (Coltelli et al., 2018)

The blown film extrusion is used for the production of pouches, industrial bags or packaging films for shrink-wrapping, because the produced film is tubular. The equipment consists of an extruder equipped with an annular die. The blown film process involves the biaxial stretching of annular extrudate to make a suitable bubble according to the product requirements. During this film-blowing process, the molten polymer from the annular die is pulling upward applying the take-up force; air is introduced at the bottom of the die to inflate the bubble and an air ring is used to cool the extrudate. The nip rolls are set to provide the axial tension needed to pull and flatten the film into the winder (**Figure 15**). (Coltelli et al., 2018)

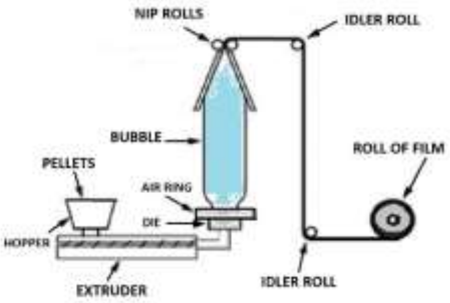


Figure 15 Schematic diagram of the blown film process (Coltelli et al., 2018).

Melt rheological properties are an important parameter to determine the processability, shape and stability of the film bubble and the onset of surface roughness.

PLA-based materials show generally a melt fluidity too high to be processed with common blown film extrusion devices. Usually chain extenders are used to improve the viscosity of the melt and the melt strength to allow the production of PLA films by blown film extrusion. Lazzeri et al., 2013 drafted a patent to produce transparent PLA-based blends containing an epoxidized molecule acting both as plasticizer, compatibilizer and fluidity regulator, thus allowing a good control of processability. With respect to traditional polyolefins, the tearing strength of films made of PLA-blends is lower. Recently it was evidenced that by using the epoxidized molecules in combination with a nucleating agent it was possible to improve the tearing strength of the PLA-blends reaching values comparable to those of PP (Coltelli et al., 2018).

5.2.2 Processing for production of rigid packaging

For the production of plastic rigid containers either the injection moulding or thermoforming (**Figure 16**) technique are used.

In the injection moulding process, polymer granules are melted in a heated barrel and injected into a mould to produce pieces with a defined shape. The automation of the process allows for series production. This method can be employed for example for producing caps, thick jars for cosmetics, cutlery and coffee capsules. (Cinelli et al., 2018) A very low viscosity at a high shear rate is required in order to grant a rapid and perfect filling of the mould. The melt flow index determination at the same temperature of injection moulding can be a useful parameter in this process and generally, thermoplastic polymers having melt flow index above 10 g/min are suitable for injection moulding. Temperature of the mould, the holding pressure and time are the parameters that are important to be controlled.

Biopolymers such as PLA and PHA can crystallize during the holding step, so the temperature of the mould and the holding time are important to allow the material to reach the desired crystalline morphology, as the amount and distribution of crystals in the material influence its final properties. (Cinelli et al., 2018)

In contrary to the injection moulding, trays, plastic cups, blisters and jars are produced by another important processing method, namely thermoforming (**Figure 16**). First, a flat die extrusion step is necessary for producing polymer sheets that are able for the thermoforming process. The polymer film with a thickness in the range of 50 - 300 microns is used for the thermoforming process. The material is heated above its glass transition temperature but below its melting point, thus obtaining a softened sheet usually by using infrared heaters. Then, a mould is inserted (or a vacuum is applied), which gives the softened sheet the desired shape (**Figure 16**). (Cinelli et al., 2018).

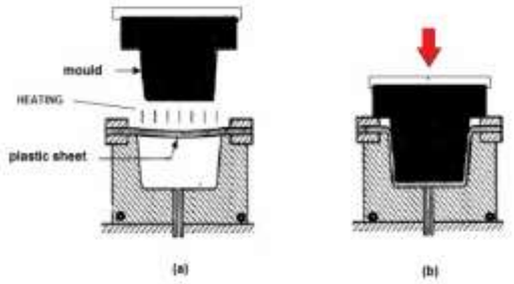


Figure 16 Thermoforming process (Cinelli et al., 2018)

6 Multifunctional coating solutions with tailored properties for packaging and textiles

Protection against oxygen is a key factor for sensitive/fresh food, cosmetic and pharmaceutical products to achieve a sufficient shelf life. Otherwise colour or taste deviation, oxidation of grease, formation of microorganisms or degradation nutrients may take place. To achieve low oxygen permeability co-extruded or laminated multilayer plastic films are widely used in the packaging industry whereby mineral oil derived EVOH, or PVDC, are the mostly used oxygen barrier materials. However, theses polymers are neither biodegradable nor bio-based. Therefore, research on sustainable packaging materials with appropriate barrier properties is underway and summarized in the following chapters.

6.1 Whey protein based films and coatings

In recent European projects (WHEYLAYER 2, no date), (ThermoWhey, no date), oxygen barrier coatings based on whey protein have been developed. Whey continues to be a widely available and underutilized (only 40% is valorised and a much lower amount would in fact allow substituting all EVOH for packaging worldwide) by-product from cheese making containing around 13% protein in dry matter. The whey protein-based coatings are formulated using Whey Protein Isolate (WPI) as well as bio-based plasticizers and/or reactive additives such as urea to enhance thermoformability. The whey formulation is subsequently coated on a plastic substrate and dried. In this process step the protein is denatured in order to form a crosslinked network. This patented step is necessary to achieve an oxygen permeability as low as 1.5 $cm^3/(m^2*d*bar)$ (Q100). (WO2,013,014,493)

Finally, the coated film is laminated into the final structure and eventually additional conversion processes such as thermoforming, sealing etc. can be carried out to obtain the packaging items. Application of both standard and thermoformable whey coating formulations have been proven in pilot scale in roll-to-roll lacquering and lamination lines. Resulting films were reported to have excellent mechanical as well as gas and UV barrier properties, beyond most existing biopolymers (**Figure 17**). Whey coatings are thus capable of replacing synthetic oxygen-barrier layers such as EVOH in multilayer packaging. Furthermore, the whey coating is both bio-based and biodegradable. Other than in untreated condition, WPI is not soluble in water due to denaturation and crosslinking in the protein structure.

On PLA, based on preliminary tests, barrier improvement factors (BIF) 6 were obtained by WPI coating. Although further tests are needed to reach the full potential of the whey coating on this substrate as its intrinsic barrier calculated on PET should have led to a 60 fold improvement vs. PLA. The use of such nitrogen rich materials protein coatings on biodegradable based films will not compromise biodegradability but in fact even accelerate it (Cinelli et al., 2014). Thus, whey protein-coating, which are in market introduction phase, represents a new application for an agro-food industry by-product while safeguarding the performance and enabling the recyclability of multilayer films which are generally landfilled. Additionally, the whey protein-based coatings used in multilayer laminates fulfil the requirements of European Commission Regulation (EU) No 10/2011.

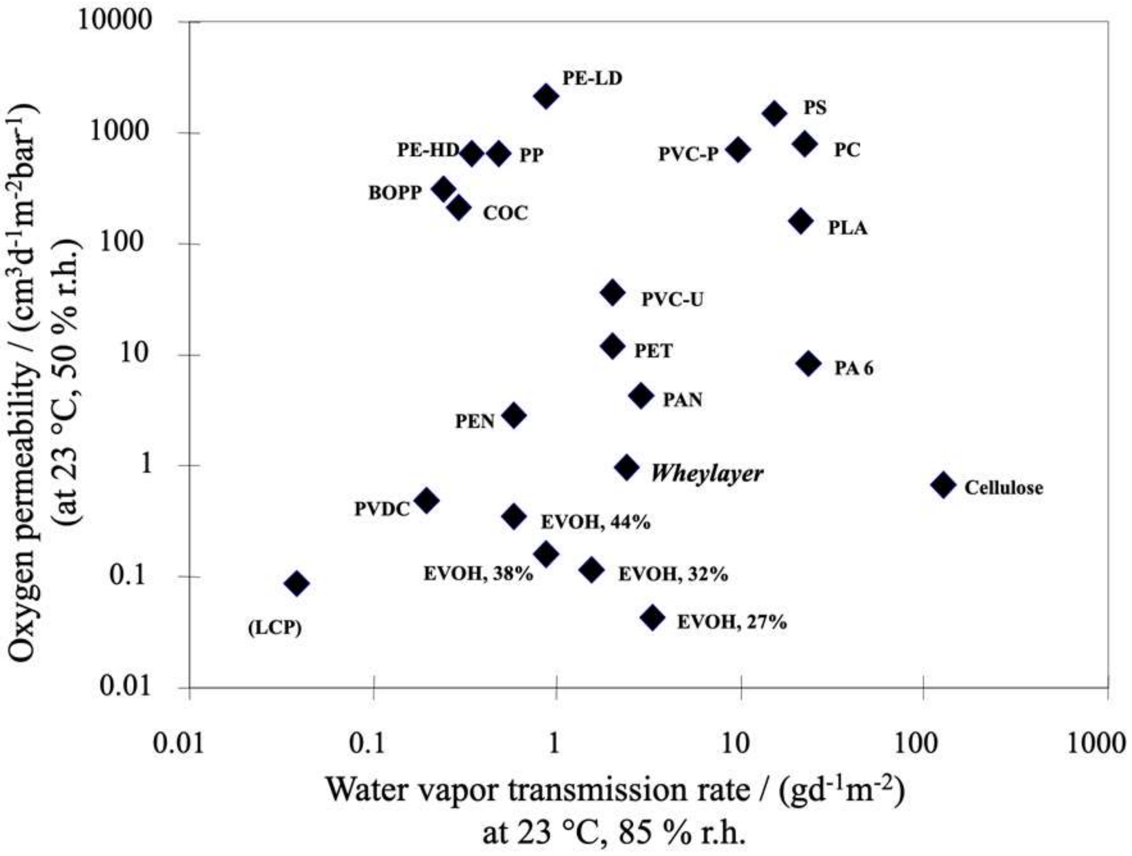


Figure 17 Permeability values of typical plastics, bioplastics and Wheylayer (Schmid, Dallmann et al., 2012; Schmid and Müller, 2019)

6.2 Other bio-based films and coatings

In addition to whey proteins, other proteins or even polysaccharides have also proven to be an effective alternative as coatings and films.

As polysaccharide, alginate is widely used in industry for food, beverage, textile, printing and pharmaceutical product as thickening agent, stabilizer, emulsifier, chelating agent, encapsulation system, swelling or suspending agent or used to form gel, film and membrane. Sodium alginate is the most common salt of alginate. It is commercially available and can be applied as coating material to serve as aroma and oxygen barrier for products with low relative humidity. (Jost et al., 2014)

Similar to whey protein and soy protein, pea protein isolate also consists of a large number of globulins, however, having a different amino acid composition. This leads to the fact that based on the proteins' source, the protein film varies in structure providing different oxygen permeability (Chang et al., 2019; Zink et al., 2016). The major components of wheat gluten protein are prolamin (gliadin) and glutenin. Prolamin has the property to dissolve glutenin, which explains the high viscosity of gluten. The firmness and elasticity of gluten films are mainly formed by glutenin. (Zink et al., 2016) Films that are made of plant protein isolates have excellent oxygen barrier properties due to their polar nature and crosslinked polymer network, however, the water vapour barrier is low. Chang et al., 2019 showed that using whey or pea protein isolate film coatings decreased oxygen permeability of multilayers. A multilayer PET/WPI/cast polypropylene (CPP) package achieved 90 times lower oxygen permeability compared to a PET/nylon/CPP control package. (Chang et al., 2019)

To overcome the low water vapour barrier of (plant) proteins, polar substrates are generally combined with hydrophobic layers, such as polyethylene layers, via wet lamination (with adhesives), extrusion lamination (without adhesives), wet and extrusion coating (please also see multilayer films in **chapter 8**). In the "wet" processes, water borne options are favoured for environmental reasons. As additional layer also waxes, starches or poly(vinyl alcohols) were studied to enhance the water vapour barrier. In addition, physical, chemical and biochemical modifications can be applied to improve the barrier properties of protein films and coatings outlined in the following **chapters 6.3, 6.4, 6.5**.

Side stream products, for instance from food processing are of high value to be used as new raw material. For instance, a moulded pulp material was recently patented to be useful as biodegradable packaging material. The patent filed a method to use the aliphatic polyesters present in the moulded pulp and a cellulose-based laminate layer to produce a compostable food packaging unit. (WO2019190324A1) Another new approach used potato starch as raw material to develop new packaging materials. The BIOPLAST products developed by BIOTEC can be obtained at different purities of bio-based carbon content that determined if the potato starch packaging material can be composted industrially or at home. (BIOTEC - Nachhaltigkeit, 2019)

6.3 Physical Modification

Heat treatment can change proteins' structure and the aggregate may be formed. This change leads to inter- and intra-molecular interactions and the formation of water and disulphide bonds formed by cysteine residues. The tensile strength of whey, soy, and gluten protein films usually increased considerably with increasing amount of disulphide bonds. Thus, the heat treatment determined the properties of the protein coating. (Fachin and Viotto, 2005; Nicolai et al., 2011; Nicorescu et al., 2008) For instance, whey protein films revealed a higher tensile strength and increased rigidity due to water removal when heating the whey proteins. At the same time, heated whey protein films showed lower oxygen permeability. (Hong and Krochta, 2006; Pérez-Gago and Krochta, 2001; Simelane and Ustunol, 2005)

Treatment with ultrasound, which is an acoustic wave with a frequency above 20 kHz, is another physical method that influences protein coating.s (Corso, 1963) Studies with frozen fish have shown that the exposure of whey protein coatings to ultrasound had a positive effect on lipid oxidation from the product, but no sensorial changes. (Kadam et al., 2013) A low frequency ultrasonic treatment of soy proteins was shown to result in a higher solubility. Both effects led to an improved vapour and oxygen barrier of the treated soy protein coating compared to the untreated soy protein coating. The changes are triggered by formation of free hydroxyl groups. Improved rejection of water by ultrasound treated soy protein coatings is explained by the higher density of this coating that was induced by cavitation. (Zhou et al., 2009)

Ultraviolet and γ-irradiations also have an influence on the structure of proteins. The irradiation is absorbed by atoms and molecules and converted into chemical energy. Under UV irradiation, the dissolution of aromatic rings and double bonds leads to the formation of free radicals in amino acids, which leads to the formation of intermolecular covalent bonds. (Gennadios et al., 2008; Rhim et al., 1999) Thus, irradiation of protein films led to an increase in tensile strength without affecting the barrier properties of the protein film. The higher the dose of irritation, the greater the changes in soy and the whey protein structures. (Ustunol and Mert, 2006)

6.4 Chemical modifications

In the case of chemical modifications, the protein to be used must be considered. The graph below provides information on the composition of individual proteins and the possible modifications.

Table 6.1 Reactive groups of different proteins and common modifications (Hammann and Schmid, 2014; Kester and Richardson, 1984)

Side Chain	Amino Acid	Commonly Used Modifications	ß-Lactoglobulin (Whey Protein) (mol %)	ß-Conglycinin (Soy Protein) (mol %)	γ -Gliadins (Wheat Gluten) (mol %)
Amino	Lysine	Alkylation, Acylation, Succinylation	10.5	6.1	-
	Arginine	TG*	2.5	8.3	1.8
Carboxyl	Glutamine	Amidation, Esterification, TG*	11.2	-	-
	Glutamic acid		6.2	24.5	45.8
	Asparagine		3.1	12.0	2.9
	Aspartic acid		6.9	-	-
Disulfide	Cysteine	Reduction, Oxidation	2.8	0.03	-
Imiazole	Histidine	Alkylation, Oxidation	1.5	2.8	1.6
Indole	Tryptophan	Alkylation, Oxidation	2.0	-	-
Phenolic	Tyrosine	Acylation, electrophilic Substitution	3.6	3.5	3.5
	Tryptophan		2.0	-	-
	Histidine	-	1.5	2.8	1.6
	Phenylalanine	-	3.2	5.4	5.2
Sulfhydryl	Cysteine	Alkylation, Oxidation	2.8	0.03	-
Thioether	Methionine	Alkylation, Oxidation	-	-	-

* Transglutaminase crosslinking: Isopeptide bonding between glutamine and lysine

Alkylation describes the replacement or addition of alkyl groups to the amino groups by lysine, which is essential for alkylation. Acylation describes the addition of acyl groups and occurs only when the protein has a nucleophilic amino acid residue that is able to react with a carbonyl group of an agent. (Kester and Richardson, 1984) A special form of acylation is acetylation. Acetyl groups are introduced into compounds which contain amino, hydroxyl and thiol groups. Basic or acid catalysts accelerate the process. Acetic anhydrides are used for acetylation. This leads to the formation of covalent bonds between amino and acetyl groups. (Hammann and Schmid, 2014) Kester and Richardson, 1984)

Succinylation is used to modify proteins on the amino acid lysine. In general, succinylation led to improved solubility of proteins, (Belitz et al., 2008) and also enhanced functional properties such as foaming properties as well as emulsifying capacity. (Franzen and Kinsella, 1976)

6.4.1 Surface modifications by chemical grafting with fatty acids

An innovative approach to improve the water vapour barrier properties of bio-based films and coatings, namely the green chemical grafting technology using fatty acids from renewable resources (using palmitoyl chloride as benchmark and the fully bio based fatty acid anhydrides) to monomolecular graft a hydrophobic layer such as the protein films (Samain, 2002). The modified protein films by fatty acids are expected to provide significantly improved barrier properties towards water vapour. Preliminary experiments at the Albstadt-Sigmaringen University showed that water vapour barrier properties of whey protein-based coated films can be significantly improved by this grafting process. The chemical grafting will be applied on protein based films and coatings by the so-called transfer method which was developed for the surface grafting of PVOH-based films. (Schmid, Benz et al., 2012) (Schmid, Sängerlaub, Miesbauer et al., 2014); (Haas et al., 2017)

The diffusion of the reagent is decisive for the transfer method. In the first step, the liquid reagent is finely distributed on the surface to be treated. The reaction is influenced by an inert, hot gas. The reagent migrates into the surface by the adsorption-desorption mechanism. During the diffusion of the reagent into the solid surface, grafting occurs. The reagent reacts with the free hydroxyl groups of the surface to be treated. The resulting by-products are continuously removed by the gas flow. (Stinga, 2008) This method, in which the substances and surfaces are esterified, is already known to improve the hydrophobicity of cellulose and starch. The application of this method can be used for many purposes. These include the reduction of water vapour absorption and the improvement of the thermoplastic properties of wood.

The main attractions of this solvent free grafting process are its low cost, its use of existing industrial bio-based reagents and its potential to be applied on a printing machine at high speed and high efficiency. It is also a clean chemistry process that does not give rise to by-products or to polluting effluents. In addition, the FA green grafting provides easy emptying properties due to significantly reduced surface energy of the grafted surfaces. These rebalance properties are comparable to emerging non bio-based market available solutions such as LIQUIGLIDE™ developed by the Massachusetts Institute of Technology or Toyal Lotus® developed by Toyo Aluminium K.K. or AsahiGuard E-Series developed AGC Chemicals. By grafting itaconic anhydride to PLA via a melting free radical grafting reaction, the grafted PLA was patented to be used to enhance the adhesion properties and thus the mechanical properties of of polyester-based composites. (CN107698714A)

6.5 Biochemical Modification

The biochemical modifications are based on the use of enzymes. The cleavage of peptide bonds is the main task of these enzymes. In addition, they influence transfer reactions as well as redox reactions and crosslinking. (Belitz et al., 2008)

In addition to treatment with FA, the use of transglutaminase to improve the properties of the protein film is the most promising one. The enzyme transglutaminase starts the process of acyl transfer responsible for the formation of covalent bonds between proteins, peptides and primary amines. (Ichinose et al., 1990)(Schmid, Sängerlaub, Wege et al., 2014) The use of transglutaminase for protein based film formation was previously investigated (Di Pierro et al., 2006; Hernàndez-Balada et al., 2009). By the use of transglutaminase crosslinks in the protein structure were formed. This improves not only the oxygen and water vapour permeability, but also the light transmission rate leading to transparent films. Hydrolytic cleavage separates proteins into their components, i.e. amino acids. The enzymes, which cause the splitting of proteins in a substrate-specific way are also known as peptidases. There are two types of peptidases which show different effects. While exopeptidases catalyse the cleavage of amino acid compounds, end peptidases have the task of inducing the cleavage of non-terminal amino acids. (Belitz et al., 2008)

The cleavage of the peptide compounds reduces the molecular weight, which reduces intermolecular interactions and leads to a higher flexibility of the molecular chains. The severity of the hydrolysis is formed from the number of cleaved compounds measured against the total number of all bonds. The higher the degree of hydrolysis, the smaller the protein fragments. Studies on coatings made of whey proteins have shown that the mechanical properties, especially tensile strength, decrease with increasing hydrolysis, while the barrier protection was maintained. (Sothornvit and Krochta, 2000; Verbeek and Berg, Lisa E. van den, 2010)

The use of nanocomposites and films from proteins results in significant differences. For instance, it was found that the treatment of a WPI film with nanocomposites such as Ti02 better blocks incident light and UV radiation. In addition, elongation and tensile strength increased, with the moisture barrier decreasing. (Li et al., 2011; Zhou et al., 2009) Furthermore, studies with montmorillonite nanoclay (MMT), another bio nanocomposite, showed that the mechanical properties of the biopolymers are improved by addition if a MMT layer. Compared to the untreated soy protein isolate films, an improvement in water vapour permeability, tensile strength and elongation at break could be achieved. Since the moisture absorption does not provide satisfactory results here either, further investigations with soy protein isolate and starch nanocrystals were carried out. This made it possible to produce a film having a lower affinity to water. (Fornes and Paul, 2003; Kumar et al., 2010a; 2010b; Zeng et al., 2005)

In addition to WPI and soy protein isolate, films can also be produced from wheat gluten proteins. Their properties are improved by the use of MMT nanocomposites. Due to the restructuring of the proteins, the water sensitivity of the films was strongly decreased. (Tunc et al., 2007)

A further biochemical modification can be achieved by the inclusion of other substances. The growth of inoculant bacteria can be reduced by the addition of antimicrobial additives. This is very promising in the development of new packaging concepts. Although the growth of pathogenic microorganisms can be controlled by the addition of antimicrobial substances, difficulties arise in the mechanical and optical properties, which are negatively influenced by the addition. (Banerjee and Chen, 1995; Hotchkiss, 1995)

In addition to bioactive proteins such as lysozymes, essential oils and nisin also possess antimicrobial properties, which have already been investigated. (Dangaran and Krochta, 2009; Min et al., 2005; Pintado et al., 2010; Seydim and Sarikus, 2006) In experiments with bilayers consisting of soy protein isolate and PLA, antifungal and antimicrobial substances such as natamycin) and thymol were added. The results showed that with antimicrobial agents treated films had a higher transparency and adhesion strength than native PLA and soy protein isolate layers. The addition of the antimicrobial substances meant that no growth of mould, yeast and two bacterial strains could take place. (González and Alvarez Igarzabal, 2013)

The addition of lipid materials also has positive effects on protein based films. Due to the high water transmission rate of protein films, hydrophobic substances such as wax or lipids can be used to increase the barrier properties. (Banerjee and Chen, 1995; Dangaran and Krochta, 2009) Studies with beeswax and acetylated monoglycerides on whey protein film confirmed a significant improvement of the WTR. However, the addition of wax or lipids resulted in decreased mechanical properties of the protein film, such as tensile strength and elongation. (Pérez-Gago and Krochta, 2001) The use of lower concentrations of lipid and wax with smaller particle sizes improves the protein films. However, the moisture barrier of protein films with lipids is lower compared to synthetically produced materials. (Shellhammer and Krochta, 1997)

6.6 Production and functional coatings for textiles

PLA coatings for textiles were previously summarized in **chapter 3.1**. Coatings are used on textiles for a number of aesthetic and functional purposes and are generally based on non bio-based materials such as polyurethane and polyamide. There are multiple applications of PLA coatings. Indeed, PLA has an excellent UV-stability and decent flame retardance properties which makes it applicable for interior and exterior applications for a broad range of items. There are several initiatives to develop PLA coatings for textiles, but so far, PLA coatings are not commercially available. One of the main reasons why PLA coatings have not yet reached the market is their brittleness. This is due to the high molecular weight of commercial PLA (ca 100.000 g/mol) vs. what is needed (ca 10.000 g/mol) for coatings. As a result, the coatings need the addition of plasticizers as can for example be seen on from partner CTB. Therefore, like for compounding, developers of PLA coatings need to look into most suited environmentally friendly (preferably bio-based) molecules available to plasticize PLA. Plasticizers are not always compatible with PLA and there may be issues with migration of the plasticizer. This causes not only increased brittleness over time but also an unpleasant feeling of the coating. Migration of the plasticizer can be limited using highly compatible molecules and/or grafting them on PLA.

7 Recyclability, Biodegradation and Environmental impact assessment

7.1 Life cycle sustainability assessment

The sustainability of a product depends on many factors: from functional to aesthetic properties, from environmental to economic and social benefits, impacts and costs, from production to end-of-life processes, and from local to global scale effects. Perfect sustainability is difficult, if not impossible, to achieve. There is always room for improvement. Ideally products are based on renewable resources, are easy to reuse and/or recycle within the Technosphere and the Biosphere and create added value without causing adverse effects to our environment and population while still maintaining a healthy profit for all supply chain actors. Bio-based, biodegradable packaging materials can meet several of these requirements. In fact, they were used widely across the globe until petrochemical based plastics took over in the 20th century offering more convenient solutions, more advanced functional properties, and/or lower production costs. Renewable resources were replaced by non-renewable, fossil resources and end-of-life recycling scenarios were substituted by incineration, landfilling, and massive littering of slowly or non-degrading plastic waste. The demand for more sustainable alternatives increased as the environmental problems of fossil based plastics became apparent. For some applications a move back to more traditional packaging materials such as paper and cotton bags or glass or metal containers is perfectly acceptable. Others require functional properties, production or modification processes that are difficult to realize with traditional solutions or that are much more easily and economically achieved with plastics. Bio-based, biodegradable plastics could meet some of these demands and can be produced out of a broad range of feedstocks including maize, potatoes, sugarcane, cellulose, tomatoes, soy, and so on (Montanari et al., 2017). (Abdul Khalil et al., 2016) (Leceta et al., 2014) (Jabeen et al., 2015) (Hottle et al., 2013; Thakur et al., 2018) (Spierling, Knüpffer et al., 2018; Spierling, Röttger et al., 2018) (Wróblewska-Krepsztul et al., 2018) (Álvarez-Chávez et al., 2012)

Publications regarding social and economic issues of bio-based plastics are fairly scarce. So conclusions regarding the overall sustainability of bio-based plastics are difficult to draw (Spierling, Knüpffer et al., 2018). This is made even more challenging due to the use of different impact assessment methods and scopes and the use of outdated information (European Commission, no date). Environmental impacts were studied more frequently and following more standardized approaches, especially in terms of global warming. Other environmental issues such as eutrophication, ozone depletion, etc. were often neglected or suffer from the use of very diverse impact assessment methods across studies.

Several bio-based materials, including bioplastics, are considered competitive to conventional plastics in terms of global warming impacts (Detzel et al., 2015; Spierling, Knüpffer et al., 2018). In case of PLA, this feat was not only achieved by production process optimizations, but also by switching to renewable energy sources to power the production system (Vink et al., 2007; Vink and Davies, 2015). As bio-based production systems do not necessarily require fossil feedstocks, fossil carbon emissions are not inherent to the system and can be avoided by switching to renewable energy sources across the supply chain.

The production of bioplastics can be carbon neutral or even carbon negative because of the uptake of carbon dioxide from the atmosphere during plant growth followed by short- or long-term carbon storage in the product. For example, the Ingeo PLA biopolymer is associated with an uptake of around 1.8 kg CO_2/kg PLA (Vink et al., 2007; Vink and Davies, 2015). Because of this carbon uptake, the cradle-to-factory gate carbon footprint lies around 2 kg CO_2 eq./kg PLA. With credits for using wind energy instead of fossil fuels, the carbon footprint of the production process is almost entirely neutralized. Technological improvements could further reduce resource needs, eventually reaching a negative cradle-to-factory gate carbon footprint in which more carbon is taken up by the plants than emitted during the production processes (Vink et al., 2007).

The total impact of a product also depends on its use and end-of-life phases. The use phase depends very strongly on specific product characteristics and regional factors. The impact of the end-of-life phase is often uncertain because of differences between what is feasible or intended by the product designer and actual, real world practices (European Commission, no date; Spierling, Röttger et al., 2018). Until now, the most common waste management approaches for bioplastics are mostly similar to those of conventional plastics: incineration (with or without energy recovery), landfilling, and recycling or composting (European Commission, no date; Spierling, Röttger et al., 2018). The dominant end-of-life approach varies by region. For example in Germany biodegradable plastics are mostly incinerated (with energy recovery) and composting is uncommon as most of the bioplastics are treated as contaminants in sorting facilities (Detzel et al., 2015). Because the market share of bioplastics is still small, no specific large scale sorting or recycling plants were constructed although mechanical recycling is associated with better carbon footprint results than the other end-of-life scenarios. E.g. recycling PLA causes the emission of 0.62 kg CO_2 eq./kg PLA compared to around 1.5 kg for composting, 1.6 kg for landfilling, 1.7 kg for incineration, and 2.2 kg for anaerobic digestion. Even when taking into account credits for energy production or material substitution, mechanical recycling remains the most climate friendly option. Taking the external advantages into account, anaerobic digestion and incineration perform better than composting and landfilling (Spierling, Röttger et al., 2018). In general, landfilling, incineration and composting are associated with higher carbon footprints than recycling due to the need for more virgin feedstocks and the conversion of the bioplastics into CO_2 and CH_4 emissions. However, more research is needed to identify the best waste treatment scenarios for bioplastics as little is known about the technical qualities of the secondary bioplastics after one or more recycling cycles. This plays an important role in the value and carbon credits associated with the substitution of virgin materials (Spierling, Röttger et al., 2018). In most cases composting performs worse than incineration with energy recovery. Composted biodegradable plastics do not deliver nutrients or structure building materials as they are practically entirely converted into CO_2 and water, so no credits can be assigned. Also, the amount of direct biodegradation emissions should be investigated further, as for example the rate of PLA degradation in composting varies a lot between studies. The end-of-life scenario in which bioplastics are fermented and converted into biogas in conventional anaerobic digestion plants needs further research and optimization before large scale application can be considered feasible (Detzel et al., 2015). Lastly, there is very little information available about littering, although it could be the most important environmental concern for plastics. The amount of plastics littered and their impact on the environment are still largely unknown (European Commission, no date).

Land use is another factor of uncertainty concerning bioplastics. Is the cultivation of raw materials for bioplastics competing with growing food, other crops such as wood, or nature? Is extra land needed for the expected increase in the production of bioplastics (Pilz et al., 2010)? For the impact calculation of Ingeo PLA no land change was taken into account because the arable land had already been in use since a long time. This neglects the fact that the land could still be used for other purposes. Furthermore it is assumed that the percentage of the arable land use is very small, even with a tenfold increase of production capacity (Vink and Davies, 2015). At this moment the production of bioplastics uses less than 0.02% of the total amount of arable land. Therefore no important competition with other crops is assumed (European Bioplastics, 2019a). The production of biomass feedstock requires more land than fossil fuel extraction, but the impact on the land could have very different proportions. In most cases the impact is less than 10% of the total cradle-to-grave land use impact (European Commission, no date). So, at this stage, it seems that the impact on land use is limited. But there is still a lot of work to be done to fully model the impact of specific land use changes on the environment (European Commission, no date).

Besides the production of the raw materials and their end-of-life fate, material properties and product design also play important roles for the environmental impact of bioplastic based products. For example, PE waste bags are associated with a lower environmental impact for several impact categories investigated (including climate change) than biodegradable waste bags containing 40-70 % fossil raw materials because of the greater thickness of the biodegradable bags. Also, for carrier bags the standard PE-HD bags have environmental advantages over bioplastic bags made from a blend of EcoFlex, PLA, and calcium carbonate because of the larger weight of the latter (16g compared to 6g) and because of the carbon dioxide and methane emissions occurring when biodegradable bags are degraded in landfills. Producing and composting biodegradable multilayer PLA films is considered more environmentally friendly in terms of climate change and fossil resources, but less so in terms of eutrophication and acidification compared to producing and incinerating multilayer PP films. Other multilayer films studied for inner or outer packaging show in most cases no ecological advantages over the reference fossil-based films. Future technological progress could reduce the environmental impact of biodegradable films down to levels comparable or lower than those of conventional ones. PLA pots and cups have been compared with PS, PET, and PP counterparts. In these studies, the weight and the waste treatment were often different. In most cases the PLA pots and cups perform better for climate change and fossil resource depletion, and worse for acidification and eutrophication. There was more variation for other impact categories. Also, for hinged PLA bowls there were no clear advantages compared to PET, PP, and PS bowls. Foamed starch loose-fill packaging has been compared with PS packaging. Some categories show advantages for the starch packaging, while the PS packaging perform better in other categories (Detzel et al., 2015).

The European Commission performed a comparative environmental impact evaluation of beverage bottles (bio-based PET compared to petrochemical PET), horticultural clips (starch compared to PP), single-use cups (PLA compared to PP and PET), single-use cutleries (PLA compared to PS), agricultural mulching films (starch compared to LDPE), food packaging films (PLA compared to PP), and single-use carrier bags (starch compared to LDPE). The manufacturing phase accounts for around 50 % of the cradle-to-grave impact for all seven case-studies. The bioplastics offer environmental benefits for the categories climate change and abiotic depletion of fossil fuels. For particulate matter they perform worse. Other categories show mixed results or are difficult to compare due to high uncertainty. The study showed that the choice of end-of-life scenario has a strong influence on the results, certainly for the carbon footprint, although the results of the end-of-life phase are highly uncertain (European Commission, no date).

As bioplastics currently represent less than 1% of the total amount of plastics produced globally (European Bioplastics, 2019a), switching from fossil to bio-based plastics could be a step towards reaching the "Europe 2020" targets for GHG emissions (European Bioplastics, 2019b). However, only 4% of European greenhouse gas emissions are caused by the use of plastics (Pilz et al., 2010) of which 40% are used for packaging purposes (European Comission, 2018; Plastics Europe and the European Association of Plastics Recycling Recovery Organisations, 2018). The impact is even lower for European consumers: only 0.6% of their carbon footprint is attributed to plastic packaging materials (Pilz et al., 2010). So the potential improvement caused by a switch to bioplastics in terms of global warming is limited. When looking at a wider variety of impact categories, bioplastics are not always environmentally superior to their conventional counterparts but they are competitive in many (Detzel et al., 2015). However, research into major environmental issues such as the effects of plastic littering on our environment and health are not advanced enough to draw conclusions at this stage. So, more research is needed to provide the insight required to move towards truly sustainable solutions and bioplastics that really outperform conventional ones in the most relevant issues.

Overall, it can be concluded that bioplastics show mixed results in terms of their environmental impact compared to conventional plastics (Detzel et al., 2015). Some of the changes that could improve their environmental impact are switching to agricultural waste streams as feedstock, developing and optimizing production processes and product characteristics, and assuring the use of the most competitive end-of-life options (European Bioplastics, 2008). It is expected that future technological improvements will help to improve product characteristics, reducing the required thickness and mass of packaging materials made out of bioplastics, improving their environmental impact (Detzel et al., 2015).. There are still technical challenges related to material properties that have to be overcome to achieve this and this must be taken into account when comparing them to conventional products (Detzel et al., 2015; Spierling, Röttger et al., 2018). At this stage there are several uncertainties concerning the life cycle impacts of bioplastics. Some are linked with the methodology (e.g. the effects of land use) and others with limited knowledge due to the early stage of development (e.g. regarding degradability when composted or in landfills, recyclability, in which waste stream the plastics end up, etc.). Bioplastics show promising results and have potential, but there is more research needed to better understand their impact and further improve their environmental performance (Detzel et al., 2015) (European Bioplastics, 2008) (European Commission, no date).

7.2 Material recyclability and reprocessing

7.2.1 Sorting

The sorting of polymers is of vital importance since even very low amounts of cross contamination can ruin the entire batch. Material recycling from mixed waste plastics is challenging and based on sophisticated process chains combining different sorting steps like screening, wind sifting, NIR (near infrared) spectroscopic sorting, electro-magnetic removal of different metals and others.

Different technologies have been developed and they are already commercially available in the market for most common polymers based on X-Ray, color laser or spectroscopic techniques. An example is Eagle Vision which is able to pre-sort PET, PE, PP, PS, PVC and PLA using NIR analysis to help remove undesirable plastics from other main streams. In terms of PLA, Titech and Unisensor are commercial examples which are able to discriminate between PET and PLA with accuracies higher than 97%, which is an acceptable amount for maintaining good properties for reprocessed PET. Furthermore, a study from Tomra sorting solution conclude that automatic sorting of other biopolymers like PHB, Starch, TPS, etc. or blends is also possible by NIR.

7.2.1.1 Basic set-up and sampling methods:

7.2.1.1.1 NIR spectroscopy

NIR instrumentation is quite simple and versatile. Because of this, it can be easily adapted to a great variety of measurement scenarios and applications. The basic setup for NIR measurements consists on: i) a broadband excitation source, which is usually halogen light; ii) a spectrometer and iii) a semiconductor photodetector, generally made of an alloy of InGaAs. Optical fiber probes can be adapted to the NIR spectrometers for remote measurements. Nevertheless, such probes should have a low-OH content, in order to avoid the fiber signal in the collected spectra.

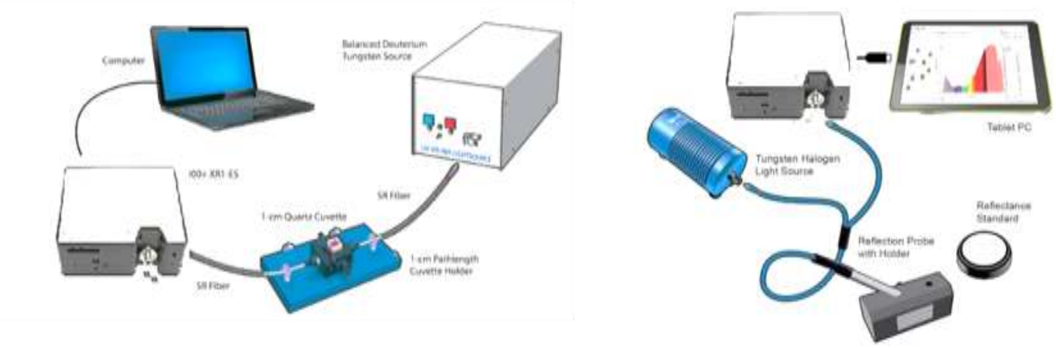


Figure 18 Experimental configurations for NIR spectrometers. a) Transmittance and b) Diffuse reflectance (illlustration from https://oceanoptics.com/determining-color-differences/)

7.2.1.1.2 Hyperspectral imaging

When imaging requirements have to be met, as often in the case of plastic sorting, hyperspectral imaging (HSI) is used. A basic hyperspectral imaging system, showed in Fig. 1, includes in its set-up, a sensitive NIR sensor; a broadband illumination source (tungsten lamps); a spectrometer, which separates the backscattered/transmitted light in its different wavelengths and, when required, depending on the configuration (i.e. for push broom configuration), a conveyor belt for sampling. In that case, it should be pointed out that the conveyor must be synchronized with the recording rate of the CCD sensor for a correct image acquisition. A hyperspectral system provides as output a hypercube. A hypercube is a group of data ordered in three dimensions, two spatial (a plane XY) and one spectral (□, wavelength), as depicted in **Figure 19**.

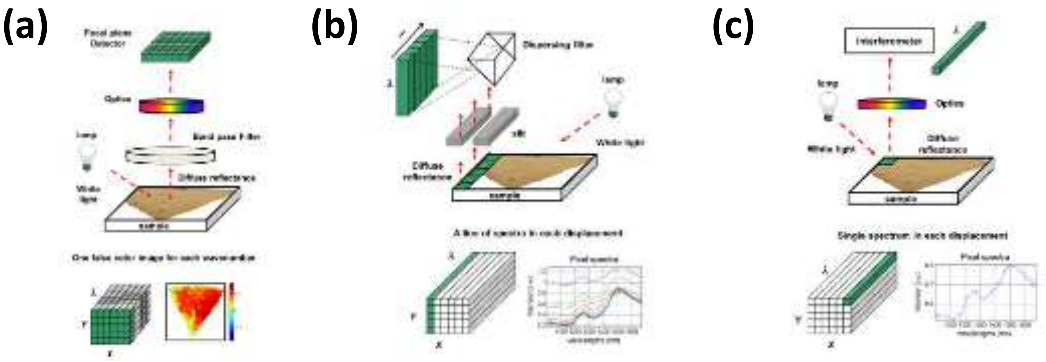


Figure 19 Most common configurations on hyperspectral devices. (a) Plane scan (snapshot); (b) Line scan (pushbroom) & (c) Point scan (Idoia, 2013)

Regarding the three configurations above, the number of pixels and as a consequence the resolution of the system increase from the system a to c, as well as the price of it and the sampling time. Nowadays, the most common configuration is the line configuration b, since it achieves the resolution needs for most applications at the same time as it offers a sampling ratio high enough for industrial applications. It is in fact the most common in plastic waste sorting which by nature generally use belts for feeding the materials.

7.2.1.1.3 Monitoring of specific parameters of PLA and derived copolymers and blends

PLA is a crystalline polymer and this property has a large influence on its properties and can also impact the ability to monitor it by HSI.

Spatial distribution of polymer crystallinity in HDPE (High Density Polyethylene), LDPE (Low Density Polyethylene) and PP (polypropylene) have been analysed by using NIR imaging (900-1700nm, 30 um spatial resolution) and chemometrics tools. (Gosselin et al., 2008) Partial Least Squares (PLS) and several pre-processing steps were applied to the NIR images to carried out to optimize the prediction capabilities of the models.

NIR imaging in combination with chemometric tools, can be used to estimate the spatial distribution of crystallinity over a sample. A step further was carried out by Ishikawa et al., 2013 when the NIR reflectance in combination with chemometrics algorithms was used to predict not only the crystallinity of PLA, but also the crystallinity of PLA/PHB blends of different ratios (100/0, 80/20, 60/40, 40/60, 20/80, 0/100) with high predictions capabilities (R^2 = 0.98) by using a SNV pretreated spectra and PLS (see **Figure 20**).

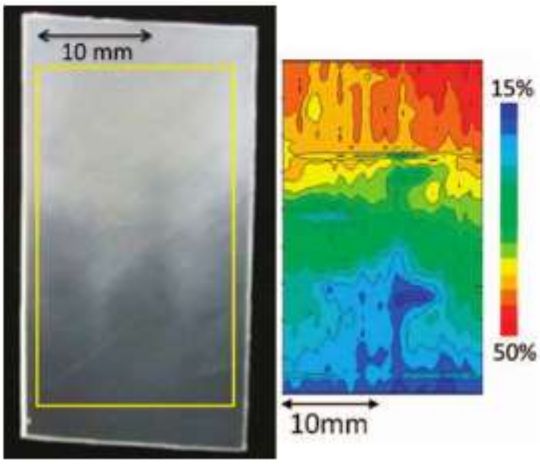


Figure 20 Optical image of PLLA sample (left), SNV treated spectra of predicted crystallinity of same chapter (right). (Ishikawa et al., 2013)

The aim of the BIOnTop project is the formulation of different copolymers to obtain bioplastics materials with improved physical properties and biodegradability. Those new copolymers are not yet commercially available so there is no study on their process monitoring. Nevertheless, the use of NIR spectroscopy have already been patented in the quantification of the amount of lactide in PLA (PURAC BIOCHEM BV, no date). Furthermore, in the literature, the use of NIR and PLS have already been successfully reported to monitor the amount of acrylate monomers in SIS-block copolymer in a the range of 0 to 30% with errors lower than 2%. (Process Monitoring by Spectroscopic Methods in the Polymer and Plastics Industry, no date)Following this procedure, NIR and Hyperspectral images will be used to quantify the ratio of co-monomers in the new BIOnTop copolymers as well as the presence of the copolymers in the end of life materials.

7.2.1.2 Sorting of multilayer plastics

In the case of multilayers, although plastic/plastic composite films are predominately incinerated, they sometimes end up in material flows of different target fractions e.g. in case there is no automated sorting or if the outer layer of a composite is thick enough to let the sorting systems identify the outer layer only. If the density of the composite material is similar to the density of the target fraction, further floatation system often in place at recyclers will not work either. As such, efforts are needed to improve the available systems for the case of multilayer recycling both through the combination of different detection techniques and enhanced data analysis. It can be facilitated using bio-based barrier materials which have very specific spectroscopic signatures vs. other plastics, such as whey protein coatings easily identified by FT-IR (Bugnicourt et al., 2013).

7.2.2 Recycling

7.2.2.1 Recycling of the monomaterials of interest

Whereas 57% of the petrochemical based PET going to bottles or containers are recycled into bottles or textiles mainly, and polyolefins as well as mixed plastics can also be commonly found in recycled grades for downgraded applications at lower cost than the virgin grades they compete with, when it comes to more speciality materials used in packaging (or even less for textiles), there is generally no current industrial solution.

For PLA organic and material recycling are possible (Figure 21). The former was considered by EU as important as the materials recycling. Recently [4] the composting was considered by EU a method of waste management identical to recycling and was defined “organic recycling”.

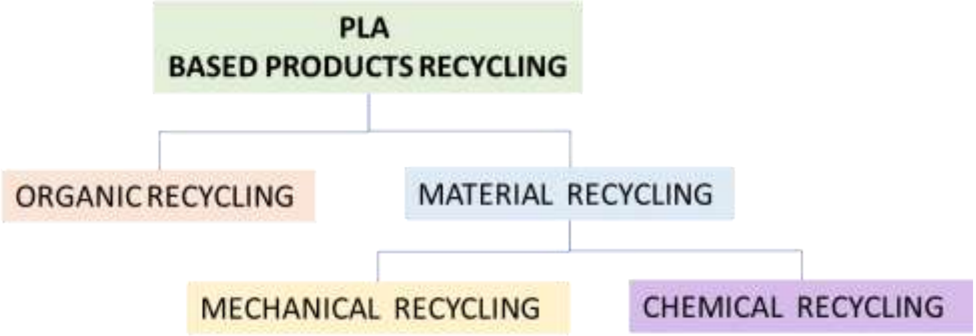


Figure 21 Scheme about PLA recycling

Regarding the material recycling, both the mechanical (based in grinding the material and reprocessing it) or chemical recycling (based on transforming the PLA in chemicals, such as lactides or oligomers) are possible for PLA. Cosate de Andrade et al. (Cosate de Andrade, 2016) recently evidenced that the material recycling is more sustainable than the organic recycling and that the mechanical recycling represents the best option in terms of Life Cycle Assessment. Hence mechanical recycling should be preferentially considered.

In general, the recycling of PLA was considered in two recent general reviews dedicated to PLA of Farah et al. (Farah, 2016) and Castro-Aguirre et al. (Castro-Aguirre, Auras, 2016). In the former it is reported that the main issue in mechanical recycling of PLA is the decrease in its molecular weight and the consequent decrease in its mechanical properties after several injections or molding processes. The major problem of recycling is the hydrolytic and thermal stability of PLA (Signori, Coltelli, 2009). Several authors (Hopmann, 2015; Elsawya, 2017) indicated the hydrolysis during processing as the main issue also in the recovery and recycling of post-industrial scraps generated during the use of PLA in packaging molding.

The hydrolysis during PLA storage must be kept also into account in view of mechanical recycling of PLA, as the recovered scraps or items necessitate to be accumulated or stored for a certain time before the successive processing. Rocca-Smith et al. (Rocca Smith, 2017) in a recent work showed that PLA films stored in different conditions of relative humidity at 50°C underwent hydrolysis in a different way. If the relative Humidity was 50% the molecular weight of PLA did not change as a function of time, but if the relative humidity was 100% a decrease of molecular weight from 70Kdalton to 10kdalton was obtained in 70 days. The result in this case is the same obtained by keeping the PLA film in liquid water. The conditions of material storage can thus affect also the recyclability of PLA.

Moreover, reprocessing of PLA induces an increase of crystallization during cooling with the number of injection cycles. Several solutions have been studied to avoid this issue mainly to minimize the PLA thermal degradation by several routes: free radicals stabilizer and reinforcement by obtaining biocomposites. Badia et al. (Badia, 2012) reported the effects of multiple mechanical recycling induced by means of five successive injection cycles on the structure and properties of amorphous polylactide (PLA). Although FT-IR analysis did not show significant changes in functional groups, a remarkable reduction in molar mass was found.

Bruster et al. (Bruster, Dubois, 2016) studied the mechanical recycling of PLA by reprocessing and identified by a multiscale approach in the case of a lab-developed grade of plasticized PLA obtained by the reactive extrusion of PLA with acrylated poly(ethylene glycol) (acryl-PEG) as reactive plasticizer. Up to 5 successive processing cycles including extrusion and compression-molding were possible.

More recently Beltran et al. (Beltran, 2017) melt compounded and compression molded a commercial grade of PLA, then subjected to two different recycling processes. The first recycling process consisted of an accelerated ageing and a second melt processing step, while the other recycling process included an accelerated ageing, a demanding washing process and a second melt processing step. Despite the degradation of PLA, the impact of the different simulated mechanical recycling processes on the final properties is limited. Thus, the potential use of recycled PLA in packaging applications is not jeopardized. This latter paper evidenced that, by well controlling the recycling procedure, the chain scission of PLA can be controlled.

In the Castro Aguirre et al (Castro-Aguirre, Auras, 2016) review the end of life scenario of this polymer is considered in all its aspects, considering also polymer footprint and LCA approach. Moreover Piemonte (Piemonte, 2011) showed, for both PLA and starch-based bioplastics and using different recycling methods (incineration, composting and anaerobic digestion), that compared with the mechanical recycling process, the other methods are clearly underperforming from the environmental point of view.

Several methodologies can be adopted to recycle PLA, to obtain different final products. The melt recycling of PLA plastic waste to produce biodegradable PLA fibers by a melt spinning process was studied by considering melt spinning quality, mechanical, structural, thermal, morphological and dyeing properties of the PLA fiber samples (Tavanaie, 2014). Based on achieved results, melt spinning of PLA fibers from recycled wastes with acceptable properties is possible. The drying pretreatment of the recycled PLA flakes, melt extrusion temperature and drawing operation were found critical for modulating mechanical and structural properties of the recycled PLA fibers.

The hydrolysis of PLA can be limited or overcome thanks to the drying. Moreover the use of chain extenders is reported to modulate the melt viscosity of PLA and its blends, as shown by Najafi et al (Najafi, 2012) that investigated the effectiveness of three different chain extenders: polycarbodiimide(PCDI), tris (nonyl phenyl) phosphite (TNPP) and Joncryl ADR 4368 in PLA and PLA-based nanocomposites containing 2 wt% clay in an effort to control thermal degradation. It was found that Joncryl was the most efficient chain extender among the ones used in this study.

However, considering mechanical recycling it is important to underline that it is necessary to have a starting material not contaminated. The contamination can be due to additives yet blended in the PLA matrix or layers. In the former case generally the compatibilization between the PLA matrix and the additive is achieved. On the contrary, when a different layer is present the successive processing must include a compatibilization strategy, as in the case of Cellulose esters as compatibilizer in wood/poly(lactic acid) composite (Takatani, 2008) or PLA/PP blends (Xu, 2015).

Chemical recycling was studied and can be a second option for PLA recycling. Due to its low depolymerization temperature and possible presence of impurity, as an alternative to mechanical recycling, PLA is a good candidate for an environmentally sound chemical recycling as it can be readily hydrolysed with water to form LA, which is then purified and polymerised to remake prime polymer (Henton et al., 2005). Controlled chemical degradation processes of commercial poly(lactic acid) in the presence of small molecules, such as diols, dipentaerythriol, diamines and adipic acid or oligo(ethylene glycol) as well as polyesterodiols were studied (Plichta, 2014). However, the most promising option could be to consider processing methodologies allowing to obtain oligomers suitable for application in adhesives or coatings (Wu, 2015).

Currently some companies dedicated to recycling of plastic materials, as ROMEI in Italy, collect and commercialize post-industrial thermoforming scraps coming from packaging companies after the necessary operations of grinding and eventually compounding. Such SRM were also considered in previous works for applications in the automotive field in the EVOLUTION project (Phuong, Coltelli et al., 2014). The use of recovered PLA in biodegradable blends or composites for durable applications thanks to reactive processing techniques is broadly considered.

The recycling of monomaterial PLA via grinding of sheets and trays, washing of the scraps, drying and the processing in extrusion machine to obtain pellets was also studied in PLA4FOOD and BIO4MAP projects (Signori, Coltelli et al., 2009). The mechanical and rheological results revealed that flowability of the melt and mechanical properties of the materials produced are maintained during several processing cycles and this assures the possibility to use recycled PLA in blend with virgin PLA without loss of material characteristics. In fact, our SME partner ROMEI already performs such activity industrially, collecting PLA scraps from thermoforming companies and reprocesses them.

Note that modification strategies such as the FA grafting (the thickness of a C16 FA grafted layer is approx. 2,5nm which would be less than 0.005% (v/v) vs. a 50 µm multilayer film) or whey protein coating when applied on rigid packaging, could still behave as monomaterials. They are for example excluded by “Der Grüne Punkt– Duales System Deutschland GmbH (DSD)” which is nowadays the leading provider of take-back systems that considers packaging as monomaterials when other materials are used in content below 5% (w/w). Indeed, such “traces” can be removed in the cleaning stages during reprocessing and do not normally harm the property of the SRM.

7.2.2.2 Multilayer packaging recycling

PET/PE bilayer, widely used for packing fresh foods could only be recycled by grinding and extrusion. As PET and PE are immiscible, their compatibility must be improved in order to employ them in high-value applications. This is possible by using proper compatibilizers (Coltelli et al., 2004; 2005; Yousfi et al., 2013) but the resulting cost is not industrially viable although some example of PET/PE recycling in highly performant technical textile applications was achieved in previous works (Schrijver et al., 2014) thanks to the application of proper REX techniques (Raffa et al., 2012; Raffa et al., 2014). Furthermore, it was observed that the degradation of the adhesive between the two layers, often consisting in poly(ethylene-co-vinyl acetate) (EVA), can result in yellowing of PET/PE blend granules (Bartoli et al., 2012), thus discouraging applications where a light colour is required.

Another example is multilayer packaging containing polyolefins and a coextruded barrier layer of EVOH that cannot be separated and is incompatible with PE and PP (Wang et al., 2007) during recycling. While flexible films cannot be recycled at all, only final recycled products with low mechanical properties can be obtained from such rigid multilayer packages (low EVOH ratio). All in all, for multilayer packaging composites, especially flexible ones, there is no high-quality recycling established currently in Europe, and most material is used for energy recovery only, which is achieved by incineration plants with an average efficiency of 35%, or landfilled depending on the country, which in both cases is counteracting current efforts towards the CE (für Umwelt and EV, 2010).

In contrast to described direct reprocessing, there are several other approaches to achieve recycling of multilayer films. One of them is the solvent based CreaSolv® technology (Mäurer and Schlummer, 2004). Specific solvents dissolve one polymer type out of the composite. A multi-step procedure separates other components of the multilayer and recovers the polymer in high purity by removal and recirculation of the solvent. Such approach is still in its industrial implementation phase. Another approach addresses the removal/dissolution of the adhesive layers of multilayer packaging. This results in separation of the components of a multilayered polymer composite but requires a subsequent separation of the segregated films by density, NIR or electrostatic. The technology is provided in technical scale by the German company Saperatec GmbH and uses a micro emulsion to separate composite films. However, the application of this concept is not yet universal, as many different adhesives are used in the multilayer market.

Likewise, the use of removable barrier layers in multilayer structures is an emerging approach to significantly contribute to increasing the recycling potential for this post-consumer waste (fig. 8) (Cinelli et al., 2016).This has already been extensively proven at TRL 4 for the whey protein coating, whereby the washing stage of the recycling process needs to be tuned to allow the hydrolysis of the whey coating using enzymes or a temperature of 30-40ºC depending on the needed process speed. This recycling approach for multilayer materials is specific to our bio-based barrier coatings but requires very little changes and investment in the recycling lines which can use their own sorting capabilities (when existing, they will only need to be tuned with the right chemometrics package to detect the new materials), shredders, washing baths, and optionally a density separation unit (e.g. in case of multimaterial structures used with the whey coating such as PET/barrier/PE) before each material can be reprocessed independently in usual compounding steps. In fact, in recent years other companies have been attempting to use this capacity to remove PVOH to claim recyclability (Nichigo G-Polymer™ Basic properties-Gas barrier performance, no date). Nevertheless, PVOH is not bio-based so it doesn't compete directly with our project but the acceptance of such new recycling approach by the recyclers could in fact be synergistic with our proposed process.

Furthermore, when applying the whey coating on bioplastic substrates (based on either cellophane or PLA), fully compostable solutions with improved barrier properties were obtained (Cinelli et al., 2014). As such our multilayer structures containing a whey protein-based intermediate layer will benefit from improved both improved material recyclability when combined with standard substrates and organic recyclability when combined with biodegradable substrates.

7.2.2.3 Coated textile recycling

Many textile materials are treated with a coating or finishing for improving material functionality. These coated textiles currently cannot be recycled because the coating layer is difficult or impossible to separate from the textile substrate material, especially as the coating layer is typically cured and therefore not reprocessable. Some possible routes are mentioned in literature such as coatings that debond upon a trigger (EP2519565A1, 2012)(EP2265681A2, 2010); (EP1814935B1, 2008); (EP1611217B1, 2007)(WO2013/189956A1, 2013) or previously mentioned Creasolv® chemical recycling based on selective extraction. These solutions are however complex, require specific sorting and handling and are thus currently not yet economically feasible. A mono-material solution (textile and coating from same polymer class) could therefore be a valuable alternative.

For specific innovative class of products, such as biobased ones, the possibility of grinding and reprocessing can be a good cheap and feasible alternative (Bartl, 2005), as evidenced previously in the case of multilayer systems. The miscibility of the polymers in the coating with the ones of the textile, the induced viscosity variations and the effect on thermal stability are the critical points to control (Harrats, 2016).

Protein based coatings are promising for modifying biobased supports (Coltelli, Bugnicourt, Schmidt, 2016) and textiles and the impact of their presence on recycling would depend on its mass percentage. Usually the coating represents a few percent of a product, hence its presence could not affect the re-processability. Nevertheless, it is necessary to consider that proteins undergo thermal degradation during processing, resulting in brown derivatives, and this can be detrimental especially considering the colour of the recycled products. Anyway, the removal of thin layer of whey protein or films consisting of whey proteins and biopolyesters from other layer (PET, PE, board, aluminium) in multilayers, with the approach of exploiting it for recycling, was considered in Wheylayer (Cinelli, Bugnicourt, 2016) and BIOBOARD projects (Schmidt, Coltelli, 2016).

7.3 Biodegradation under industrial and home composting and anaerobic conditions

Industrial compostability was the first process of organic recycling for which a test strategy including specific requirements was developed. This resulted in the harmonized EU standard EN 13432 Requirements for packaging recoverable through composting and biodegradation - Test scheme and evaluation criteria for the final acceptance of packaging (2000) according to which a broad range of products are certified. Examples of plastic materials that can be biodegradable under industrial composting conditions are PLA, TPS, PHA, PBS, PBAT… and can be found on the list of certified products of TÜV AUSTRIA Belgium and DIN CERTCO. Conventional plastics as LDPE, PP, PET are not biodegradable by micro-organism within a reasonable time frame and can as such not be treated by composting. However, engineered enzymes are developed which might make the microbial degradation of polymers such as PET possible (WO2019168811A1)(patent WO201918811A1), but research is still needed.

The biodegradation of a polymer is influenced by the exposed environment (temperature, moisture conditions, microbial population, pH, oxygen content…). A material that degrades by microbial activity under industrial composting conditions does not necessarily degrade in a home composting unit or under aquatic conditions (Narancic *et al.*, 2018). During home composting, the high temperatures (> 50°C) required by some polymers such as PLA for starting the hydrolysis and degradation and obtained during industrial composting processes, are mostly not reached. At lower temperatures, degradation rate is reduced or even limited. Therefore, in order to be home compostable, a material must demonstrate sufficient biodegradation and disintegration at ambient temperature. This principle was first applied by the OK compost HOME Conformity Mark of certification institute TÜV AUSTRIA Belgium. Currently, also the German Certification Institute has developed a logo: DIN-Geprüft Home Compostable. On a European level home composting has become an important factor in France, with the ban of conventional lightweight plastic shopping bags, the encouragement of bioplastics compostable at domestic level and the introduction of a French national standard on home compostable materials NF T 51-800 Plastics – Specifications for plastic suitable for home composting (2015). Moreover, also at CEN level a standard for home compostable carrier bags is being developed by work group CEN TC261/SC/WG2 (EN 17427). Several European companies, such as BASF, BIOTEC, LIMAGRAIN, NOVAMONT, FUTAMURA, etc. have developed polymer resins that are home compostable, but they have limited thermomechanical behaviour and processability. Most of these products are starch, polyhydroxy butyrate (PHB) or polyhydroxy succinate (PBS) based, although the Ecovio compounds of BASF contain PLA (in low amount when meeting home compostability requirements- rest being non-bio-based PBAT). On the market, there is still a lack of home compostable products meeting the needs of the packaging applications (in terms of price, controlled biodegradability and product properties). However, extensive research is performed to increase the possibilities. As an example organic coatings on basis of whey proteins are developed, resulting in higher barrier properties, while maintaining the biodegradation. (Cinelli et al., 2014) Polylactic acid (PLA) is currently the most affordable bio-based and biodegradable plastic but its biodegradability is not granted under home composting conditions. The development of a PLA that degrades under mild conditions would boost the applications for biodegradable products.

Besides, it is well known that compostability rate is thickness dependent. While it may be possible to compost a specific bioplastic sample used in packaging film, a consumer product such as thick injected cosmetic jar, made from this bioplastic may not compost at a rate sufficient to meet the compostability standard, simply because it is too thick. This is true even for starch derived or PLA based materials at high thickness used for rigid food packaging (trays). For example, PLA for industrial composting conditions is certified up to 3000 µm thickness (NatureWorks, USA), but polybutylene succinate (PBS) up to 68 µm (Xinjian Blue Ridge Tunhe Polyester Co., LTD; China) and polybutylene adipate terephthalate (PBAT) up to 120 µm (BASF, Germany). As biodegradation is also determined by the characteristics of the environment (temperature, moisture content, pH, oxygen presence, microbial population…), specific test procedures were developed to determine biodegradation of plastics under anaerobic conditions (ISO 15985). However, although AD in biogasification plants is considered in the EU Waste Directive as a valuable treatment method for organic recycling, there is currently no standard existing that defines the specific requirements on biodegradation, disintegration and effect on the digestate that should be fulfilled (EN 13432 only prescribes some general requirements for AD). AD has so far only been poorly investigated as an EoL option for bioplastics and packaging. Still, it is an interesting technology due to additional biogas formation, suitable for electricity or heat production. In fact, the bioplastics can have a positive effect on biogas production due to their high C/N ratio.

7.4 Predictive biodegradation modelling for biodegradable plastics

For predicting the biodegradation of organic compounds (chemicals), different models exist, such as BioWin and BESS. The key parameters and definition of the two mentioned models may be of interest for our current work, thus in the following we give a brief synopsis of them.

BioWin (Envirosim) is a wastewater treatment process simulator that ties together biological, chemical, and physical process models. BioWin includes a proprietary biological model that is supplemented with other process models (e.g. water chemistry models for calculation of pH, mass transfer models for oxygen modelling and other gas-liquid interactions). A stock and flow schema is used to represent the system.

BESS (*BESS, A System For Predicting The Biodegradability Of New Compounds | Research Project Database | Grantee Research Project | ORD | US EPA*, 1996) is a biodegradability evaluation and simulation system. It can predict the biodegradability of a compound based on the structural features of that compound and the prevailing environmental conditions. It builds a hierarchical knowledge based of biodegradation rules, which allow the user to ask questions such as "How does the biodegradation of compound X occur". The system includes knowledge of "first principles" on the biodegradation of different structures such as, Alkanes, Amino Acids, Monocylic Hydrocarbons and Sulfonates among other categories of structures.

Nevertheless, there is little on the state of the art of biopolymer biodegradation models given that it is a much more complex process and a field receiving emerging interest, and those publications which exist, besides those mainly related to experimental data previously covered in the deliverable, either avoid modelling or tend to be very specific(e.g. predicting land filling effects). However, in the following we summarize two works which may be relevant to our work in the BIOnTop project.

Abi-Akl et al., 2019 represents an interesting work related to kinetic models, in which the authors develop a theoretical model that accounts for the bio-chemo-mechanically coupled kinetics of polymer degradation, by considering the production of bio-degraders and their ability to both dissociate the material from its external boundaries and to penetrate it to degrade its internal mechanical properties. In the considered system, chitin particles are assumed to be perfectly spherical and composed of two species: a solid polymeric matrix and an impregnating solvent. The latter can contain, in addition to solvent molecules, dissolved monomers and enzymes secreted by bacteria living on the surface of the particle and in its bulk. They show that their model quantitatively captures the experimental results and reveals distinct signatures of different bacteria that are independent of the specific experimental conditions (i.e. degrading chitin particle volume and initial concentrations). Key characteristics include: particle radius/volume, temperature, energy, particle velocity, concentration of enzymes/bacteria, bacteria proliferation rate, time scale, and so on.

Model parameters. The exhaustive set of model parameters is: k, T, η, ψ0, N0, χ, γ, ιD, α, β. At room temperature, k and T are known: kT = 4•10-21J. Parameters η and ψ0 characterize the solvent, N0 and β describe the initial elasticity and swelling of the polymer hydrogel, γ and ιD describe the enzyme secretion and diffusion, and kinetic parameters α and β describe the degradation. All model parameters are known, except for α, β and γ, which are estimated during the modelling process for each of three different bacterial strains.

The degradation rate of the solid network is the thermodynamic conjugate of the driving force and is considered here to obey a kinetic law of Arrhenius form:

$$\dot{A} = \beta usinh\left(\frac{\eta f}{kT}\right)$$

Equation 1 Degradation rate of solid network

where the kinetic parameter β depends on the specific bacterial strain. f stands for the degradation; $f\dot{A}$ the dissipation rate per unit surface, k the Boltzmann constant, T the temperature, η the volume of a solvent unit, f the driving force on the boundary.

Now introducing A* = A / L0 and N* = N / N0, where L0 denotes a length scale of the dry particle, allows the following to be defined in dimensionless forms

$$\frac{\delta N^*}{\delta t^*} = -\alpha^* u^* N^*$$

Equation 2 Elasticity change rate (dimensionless)

And

$$\frac{dA^*}{dt^*} = \beta^* u^* sinh\left(\frac{\eta f}{kT}\right)$$

Equation 3 Degradation rate (dimensionless)

respectively, where the dimensionless parameters α* and β* are such that α* = t0αuc and β* = t0βuc =L0 . Also, u is the chemical potential per unit reference volume and f represents the driving force of dissociation on the boundary of the particle.

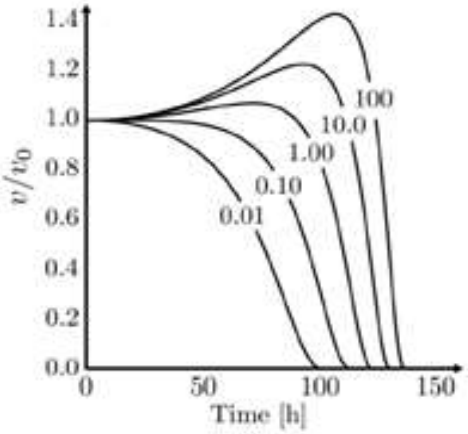


Figure 22 Evolution of normalized particle volume variation for various values of initial particle volume (expressed in 10-3mm3) containing 97% of solvent initially. Kinetic parameters are kept constant α*=1.1, β*=0.036 and γ*=0.77 (illustration from Abi-Akl et al., 2019)

On the other hand, Sivakumar et al., in (Sivakumar Babu *et al.*, 2010) propose a generalized constitutive model for municipal solid waste, based on the framework derived from critical state concepts and incorporating the effects of mechanical creep and time-dependent biodegradation, to predict total landfill compression under incremental loading and with time. The proposed model predicts the total settlement in a range similar to the reported models that consider all three components: mechanical, creep, and biodegradation of the settlement: Soil Mechanics-Based Models, Empirical Models, Settlement Models Incorporating Biodegradation. It is stated that the solubilization of organic materials is generally expressed using first-order kinetics. However, the determination of the kinetic coefficients or the hydrolysis constants as well as their variation with environmental conditions is difficult. Many fitting parameters are given which may give indirect insights on how to approach BIOnTop case. **Figure 23** shows how the proposed model is used to predict the settlement for different landfill layer (lifts) thicknesses. It was found that the lift thickness had a significant influence on the settlement behaviour.

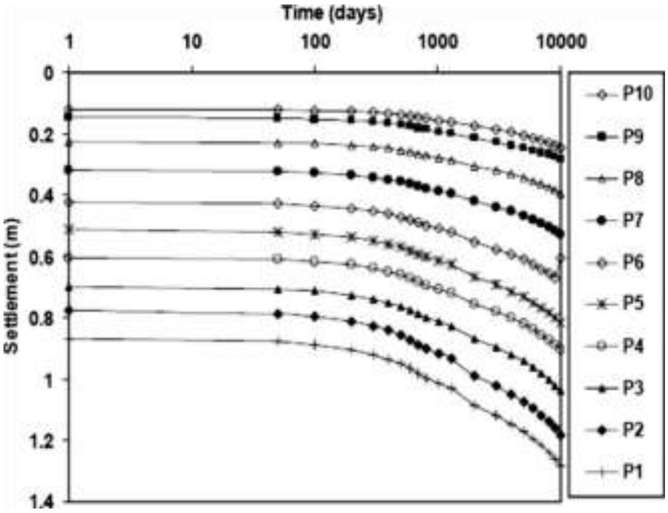


Figure 23 Effect of waste lift thickness on predicted settlement using the proposed model.

8 Bio-based mono and multilayer films and trays

8.1 Recent advances in bio-based mono and multilayer films and trays for F&V packaging, dairy and personal care packaging & multiple use shopping bags

Europe is one of the largest consumers of plastics in the world and around 40% of the material processed is used in packaging. The food packaging industry is showing an increased interest in the development of new bio-based materials to ensure that the food contained is safe and healthy and have an optimal conservation. Big brand owners have introduced bioplastic packaging, including Danone (Actimel, Activia, Volvic), Coca-Cola (PlantBottle), PepsiCo, Heinz, Tetra Pak and L'Occitane. But currently there is no market available cost-effective home compostable polymer with high bio-content that also complies with the requirements of sensitive products packaging. In 2014, 67.5% of produced biopolymers were used for packaging. The majority of the current bioplastic-packaging (86% according to EUBP data) consists of bio-based but non-biodegradable plastics such as bio-based PE and bio-based PET. However, there are undoubtedly applications where this feature is desirable (e.g. when food leftovers or material structure make material recycling non-feasible, or when collection is not properly handled). In terms of biodegradable plastic packaging, food packaging controlled more than 70% of the global market which is growing at over 18% CAGR globally from 2013 to 2019 to reach a value of $8,415.20 million. (RnR Market Research, 2019)

The market driver for growth are new packaging material developments with improved properties, greater availability and lower price, increasing awareness of environmental issues, and the adoption of new regulatory requirements. Monolayer films composed of whey gluten was recently studied by Reis et al., 2018. Whey gluten bioplastics were produced by traditional extrusion techniques and evaluated for its properties by using different pH conditions and additives (ie. Xanthan gum, glyoxal). This study revealed that mechanical properties of gluten-based bioplastic can be adjusted by pH with increased tensile strength properties at alkaline conditions (pH 9), thus enabling a suitable plastic substituent. (Reis et al.,

2018) In an EU project called FRESH, innovative cellulose-based plastic trays have been developed and produced via a lamination technology. The fibre-based packaging composite is bio-based an biodegradable. (Huhtamaki - Fresh - Huhtamaki Group)

Developments in bio-based multilayered films were done by various industries. For instance, four key players in the bioplastics industry, Eurotech Extrusion Machinery, NatureWorks, Nippon Gohsei and Sukano, developed a multilayer barrier film (Nichigo-G-Polymer) composed of PLA that is transparent and bio-based providing lower oxygen transmission rate but about 8 times lower water vapour transmission. Overall, the companies stated that thie multilayer barrier film is feasible for the production of dry food packaging. However, details about the composition and biodegradation are not given. (Sukano AG, 2019)

A multilayer film composed of polylactic acid that was coated with a silicon oxide barrier was shown to be suitable as cheese packaging material preserving its quality till 65 days and thus providing an alternative packaging material to conventional plastic multilayer films. (Piscopo et al., 2019)

Another driver for packaging innovation is the need for more reusable options such as textile based reusable food wrap which are emerging solutions consumers can tap upon as primary carrier for dry food. The global market for food wrap films was valued at US$ 10,038.6 million in 2017. The increased demand for on-the-go food across the globe is the key driver for the global food wrap films market. The market is forecast to expand at a CAGR of 2.1% during the forecast period, 2018-2026. Currently, market is dominated by aluminium and plastic wraps, together >80% of market. But the market is under pressure because of environmental concerns associated with the harmful effects of conventional plastic materials which are not biodegradable. Moreover, the main materials used nowadays pose potential health threats: (i) the toxic effect associated with plasticizers in PVC based food wrap films is hazardous for an individual; (ii) LDPE based food wrap films may contain harmful chemicals such as diethylhexyl adipate (DEHA); (iii) the direct contact of food with aluminium-based food wrap films might cause dementia and other adverse effects on the consumer health.

Besides investigations in new materials, there are also intentions to enhance the use of recycled material. For instance BASF, Borealis, Südpack and Zott developed prototypes of food packaging material made completely from recycled material. (https://www.packaging-360.com/kunststoffe/prototyp-einer-nachhaltigen-mehrschichtverpackung/, 2019).

8.2 Food packages health & safety assessment

The requirements for packaging that comes into contact with food are clearly defined by EU regulations. EU Regulation No. 1935/2004 stipulates that packaging must be manufactured in accordance with good manufacturing practice. Under foreseeable use, they must not endanger human health or cause undesirable changes in food. In addition, the sensory properties may not be negatively influenced by the materials used. (European Commission, 2004)

EU Regulation No. 10/2011 describes the limit values for the migration of monomers used for polymer based materials intended to come in contact with food. Most monomers are given a specific migration limit, which is expressed as milligrams per kilogram of food (mg/kg). If no specification exists for a material, an overall migration limit of 60 mg/kg applies. (European Commission, 2011)

Particular attention shall be paid to the manufacture of packaging material from recycled materials. Compared to packaging made of "new" materials, recycled materials are at risk of cross-contamination through prior use or unspecified use by consumers. (Welle, 2011) The EU Regulation No. 282/2008, which describes the requirements to use materials made of recycled plastics as follows: It describes that materials made of recycled plastic are only permitted if they are produced according to a specified recycling process. These processes must have an appropriate quality assurance system, which measures and monitors the defined criteria. (Vassiliou, 2008)

9 Bio-based nets and textile packaging

9.1 Recent advances in the development of bio-based nets

Nets are a widely used packaging format for fruits and vegetables. ECOBIONET project faced up the EoL treatment of plastic nets if mixed with the household waste. The management of this waste causes problems to household waste treatment due to their low apparent density and high strength (i.e. material is difficult to be cut and the nets may get entangled and collapse treatment machines). The main objective of the project was to industrialize the process and technologies related to the fabrication of different types of biodegradable compostable nets, obtained by extrusion melt spinning process (one-step process), for agriculture and shellfish packaging products. ECOBIONET goal was to manufacture completely biodegradable and compostable packaging nets while being both cost-competitive and technically comparable to current polyolefin-based nets. For this, a new biodegradable compound was obtained, derived from the synergic combination of different immiscible biodegradable polyester materials (including an important percentage of PLA) with plasticizers and compatibilizers. However, ECOBIONET nets are only completely biodegradable in the conditions of a composting plant.

So far, there are some biodegradable nets available on the market. For instance, BIO4PACK offers nets composed of starch- or cellulose-based materials that are reported to behave similar to traditional plastic nets. (Netze - Bio4Pack, 2019) Fkur produces bio-based and biodegradable nettings for example the Green HDPE SHE 150 made of high density polyethylene-green (HDPE) copolymer ethylene with 1-butene from BRASKEM (Nettings › FKuR, 2019)

9.2 Recent advanced in the development of bio-based textile fibres, yarns and fabrics for packaging

The use of biopolymers in textile applications is nowadays only via extrusion and is estimated at 100 kTon per year (European Bioplastics, 2019), which has the potential to increase strongly in the coming years if broader applicability and better price with adapted polymer formulations are achieved. PLA and PHA are the main drivers for the growth in the field of bio-based, biodegradable plastics. Currently, most used (partially) bio-based polymers are often “drop-in” variants of the oil-based counterparts such as bio-PE, bio-PET, bio-PTT, etc. Current bio-based and biodegradable textiles consist mainly of PLA (Ruys and van Olmen, 2012). TPS (thermoplastic starch) is rarely used since its mechanical properties are insufficient for most textile applications. Other (partially) bio-based materials are in research for textile applications as well (e.g. PHA, PBS, PEF and bio-PA). PLA is currently and will be in the near future the only bio-based and biodegradable polymer resulting in high-quality products which is also available in sufficient amounts and at acceptable price. However, although the feedstock is bio-based, for fully environmentally sustainable solutions, improvements are still required for EoL not to be limited to high temperature and humidity composting conditions. As other bottlenecks, PLA is more expensive than fossil-based textiles, PLA processibility is more sensitive (mainly due to hydrolysis) and a better understanding and control of the biodegradation potential are needed.

PLA fibres have a number of characteristics that are similar to many other thermoplastic fibres, such as controlled crimp, smooth surface and low moisture regain. The physical properties and structure have been studied by several researchers (Drumright et al., 2000), and suitability as textile fibre is already acknowledged. Its mechanical properties are considered to be broadly similar to those of conventional PET (Lunt and Bone, 2001) and, probably due to their lower melting and softening temperatures, comparisons to polypropylene are also appropriated (Palade et al., 2001). PLA filaments are available on an international market, but volumes are still limited. Examples of their producers include EcoDear PLA (Toray) (ecodear® Plant-based Synthetic Fiber | Our Businesses | TORAY, 2019), Biofront (Teijin Fibers), PLA filament yarn (Polisilk) (polisilk - PLA filament yarns) and Diolen(*Polyester PET - - High Tenacity*, no date) (Swicofil HT PLA). Also, PLA based textiles for clothing application are being developed(*FIBFAB PROJECT*, no date). Last years a lot of research has been conducted to tailoring the properties of PLA with additives or using PLA in a blend to suite more applications (Farah et al., 2016).

PLA-based textiles are commercially available: some examples are groundcovers for weed control, textiles for crop protection, etc. PLA-based materials are also gaining interest in textile domains like apparel and interior textiles where biodegradability is not such an issue as recycling is a more valuable EoL solution. Often these products are mainly to demonstrate the feasibility of a sustainable/bio-based product and they have so far no or only a very limited market share.

Several textiles are used in the packaging sector, such as nets, sachets, pads, etc. Mainly due to consumers' preferences in terms of convenience, as opposed to tea in bulk, individual serve tea bag is the leading format in the EU hot tea market. Tea bags were traditionally made of cellulosic non wovens with PE bags as secondary packaging. Nevertheless, improved materials based e.g. on PET are also used in new formats like pyramids. These pyramid bags are still limited in absolute numbers, e.g. €13million in Germany compared to standard bags (>€550million). However, whereas the revenue from standard bags is decreasing, the pyramid tea bag revenue increased by more than 20% from 2015 to 2016. SIOEN already supplies woven tea (pyramid) bags from PET and is also offering a bio-based alternative from PLA. However, as already mentioned, that one is not yet home compostable. To drive the application of (the slightly more expensive) PLA tea bags, biodegradation is key. Further, following the trend for minimizing packaging, by our home compostable tea bags we will remove the need for secondary packaging, that way creating a unique truly sustainable solution.

9.3 Food packages health & safety assessment for nets and textile solutions

For nets and textile packages, Regulation (EC) No 1935/2004 (European Bioplastics e.V., no date) ('the Framework Regulation') sets out general safety requirements for all food contact materials and articles which are intended to come into contact directly or indirectly with food in order to ensure that substances do not migrate into food in quantities large enough to endanger human health or to bring unacceptable change in the composition of the food or a deterioration in its organoleptic properties.

In particular, the European Parliament is implementing this Regulation with European Parliament resolution (European Parliament, no date) (6 October 2016) with the objectives to underline that the major focus should be on the adoption of specific measures for those 13 materials not yet regulated at EU level (Adhesives, Cork, Rubbers, Glass, Ion-exchange resins, Metals and alloys, Paper and board, Printing inks, Silicones, Textiles, Varnishes and coatings, Waxes, Wood) to anticipate the upcoming review by the Commission's Joint Research Centre of the national provisions adopted by Member States for non-harmonised materials, to point out that, given the prevalence of the materials referred to on the EU market and the risk they pose to human health, and in order to preserve the single market for FCMs and food products alike, the Commission should forthwith prioritise the drawing-up of specific EU measures for paper and board, varnishes and coatings, metals and alloys, printing inks and adhesives.

The health & safety risk assessment on new developed products has to be evaluated according to Plastics Regulation (EU) No 10/2011 (Ruys and van Olmen, 2012) to verify compliance with the defined limits for the Overall Migration and Specific Migration: the mass transfer properties of the selected materials using conventional and realistic methods for migration evaluation of representative molecules already present in the basic polymer(s) but also of substances not been added for a technical reason during the production process, “non-intentionally added substances”, such as impurities, reaction and degradation and decomposition products.

10 Conclusion

This deliverable summarizes the up to date state of the art of the recent advances in bio-based and biodegradable polymers. More than 240 sources have been reviewed including scientific literature, patents and commercial information. The literature compilation indicates that there is a huge interest in developing new materials for bio-based packaging and textiles and in biodegradation of these materials. In particular, lactic acid and whey proteins are highly promising and well studied polymers for bio-based packaging films that are currently studied in multilayer films or in modified versions to further enhance barrier properties. Although the mentioned and other bio-based material were extensively studied as outlined in this deliverable, more studies focusing on grafting technologies, bio-based multilayers as well as upscaling processes, sorting techniques and end of life options are still needed.

Some interests of researchers in end of life alternatives for bioplastics were also summarized. Considering post-consumer PLA based products coming from packaging, the mechanical recycling is considered the best option based on LCA studies. Potential issues and related solutions considering the different options were reviewed.

Thus, this deliverable provides a good fundament for the work packages along the project for each partner to perform their work. This reconfirmed the respective novelty of the BIOnTop project concept in each covered field. Based on this information, new material compositions and processing mechanisms can be developed avoiding duplicating past efforts.

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