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FUTUREbio

BIODEGRADABLE PLASTICS FOR A GREEN FUTURE

Project No: 2021-1-TR01-KA220-HED-000032160

EDITORS
Prof. Dr. Yasemin OZTEKIN
Prof. Dr. Ulku SAYIN

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PREFACE

Plastic is a synthetic polymer material usually produced from petrochemical raw materials. It is durable, lightweight and can be produced in various forms. Plastics have a wide range of uses and are used in the production of packaging, toys, electronic goods, and many other industrial products. They have become indispensable in modern life due to the many advantages they offer. However, due to their ability to not decompose for a long time, which can cause environmental problems, studies focusing on recycling and nature-friendly alternatives continue. In recent years, the potential to prevent these environmental problems has emerged by developing new generation materials such as bioplastic and biodegradable plastic.

Bioplastics are plastics made from biodegradable or non-biodegradable polymers, usually obtained from renewable resources. These materials may contain biodegradable polymers that can be derived from corn starch, sugar cane, potatoes, and other plant sources. Biodegradable bioplastic is plastic that can be naturally degraded by microorganisms in nature. Bioplastics can have less impact on the environment than traditional plastics, which remain intact in nature for years, especially biodegradable ones, which can decompose faster in nature. These features minimize the amount of waste and harmful effects they leave in nature and make them an environmentally friendly alternative in various usage areas.

Since environmentally friendly materials are an important factor in shaping the world in which future generations will live, further research and development is needed to ensure wider adoption of these materials in industry. On the other hand, there are some difficulties and limitations regarding the production and use of bioplastics and biodegradable plastics. Therefore, continuous research must be carried out to further advance and optimize these new technological developments.

The book ***“Biodegradable Plastics for a Green Future”***, which is the output of the project titled ***“Let’s use biodegradable plastics for the future/FUTUREBIO”*** numbered 2021-1-TR01-KA220-HED-000032160, supported by the Turkish National Agency within the scope of Erasmus+ Key Action 2 Strategic Partnership, polymers, it contains information about plastics, bioplastics, biodegradable plastics, their characterization, and applications.

We would like to thank all the researchers and authors who contributed to the book chapters. We would like to express our gratitude to the Turkish National Agency for supporting our project and the publication of this book within the scope of Erasmus+ Key Action 2 Strategic Partnership.

Prof. Dr. Yasemin OZTEKIN, **Editor**

Prof. Dr. Ulku SAYIN, **Editor**

ABOUT FUTUREBIO

You are reading the book ***Biodegradable Plastics for a Green Future***, one of the project results of the ***"Let's use biodegradable plastics for the future/FUTUREBIO"*** Project numbered 2021-1-TR01-KA220-HED-000032160 which is supported by the Turkish National Agency under the scope of Erasmus+ Key Action 2 Strategic Partnership. In the FutureBio project, in which the coordinating institution is Pamukkale University (PAU), Selçuk University (SU) and Kırklareli University (KLU) from Türkiye; Fondazione Bruno Kessler (FBK), Cosvitec Societa Consortile Arl (COSV), Universita Degli Studi Di Trento (UNITN) and Indivenire srl (IND) from Italy; Universitatea Technica Cluj Napoca (UTCluj) from Romania; CTRL Reality Oy (CTRL) from Finland; Ostbayerische Technische Hochschule Regensburg (OTHR) from Germany; and University of Applied Sciences of Southern Switzerland (SUPSI) from Switzerland are the project partners.

As it is known, plastics derived from organic materials, reusable, and biodegradable by microorganisms are an important part of environmental and sustainability strategies, but today they account for less than 1% of total polymer materials. Biodegradable polymers should be developed and used for a more livable and greener world. Reducing carbon emissions is particularly important as part of the "Green Deal" for a more livable world. Therefore, FutureBio's main goals are to promote and increase the use of organic-based bioplastics instead of conventional plastic materials, which are carbon-based and difficult to dispose of, and to raise public awareness about environmental pollution and environmental protection.

In line with these goals, efforts are being made to develop high-tech training modules for academic staff, university students, and industrial workers, organize training activities for academic staff and students, and raise public awareness.

Virtual reality applications, online and open-access course materials, and laboratory videos were produced following field research. Turkish and English electronic versions of the book ***Biodegradable Plastics for a Green Future*** are available on the project website https://futurebioproject.eu/.

With the happiness of completing our book, we would like to thank the Turkish National Agency for their support for our project. We would like to thank Prof. Dr. Ahmet KUTLUHAN, Rector of Pamukkale University, for his valuable support for two years. As Pamukkale University project team members, we would like to thank all our partners for their valuable efforts and contributions. We would also like to thank Prof. Dr. Yasemin OZTEKIN and Prof. Dr. Ulku SAYIN for editorialship of this book.

Assoc. Prof. Dr. Arzum ISITAN

Project Coordinator

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CHAPTER 1: POLYMERS

Cem Gök, Mine Sulak, Volkan Onar, Arzum Işıtan

1.1.Definition of Polymers

Cem Gök, Mine Sulak, Arzum Işıtan

Many of the terms, definitions and concepts used in polymer science are not used in other branches of science. These terms, definitions, concepts need to be understood to fully discuss the synthesis, characterization, structure, and properties of polymers. Some of these will be introduced at the outset as they are of fundamental importance, many of which will be discussed in a detailed manner in later chapters.

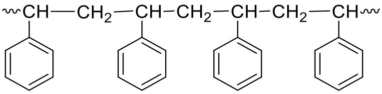
1.1.1. History of Polymers

The history of polymers dates to the early 19th century when scientists first began to study and understand the properties of long chains of molecules known as polymers. The term “polymer” was coined in 1833 by Swedish chemist Jöns Jacob Berzelius, who used it to describe the large molecules that make up many natural substances, such as proteins, starch, and cellulose. Used as a substitute for ivory in the 1870s, celluloid is one of the oldest man-made polymers. Celluloid is made from cellulose, a natural polymer found in plants, and has been used to make a variety of products, including film, combs, and billiard balls. By the early 20th century, scientists began to develop synthetic polymers or artificially produced polymers instead of obtaining polymers from natural sources. One of the first synthetic polymers was Bakelite, developed in 1907 by Belgian-American chemist Leo Baekeland. Bakelite is a thermosetting plastic, meaning it becomes rigid and inflexible when heated, making it useful for a variety of applications, including electrical insulators and jewelry. Amber and natural rubber have been known for a long time. Natural rubber was first used as an eraser in 1770, as it erased marks. Staudinger first proposed the macromolecule hypothesis in the 1920s and was awarded the Nobel Prize for its acceptance in 1930 and 1953. Flory was the first to explain the mechanism of the addition polymerization reaction and was awarded the Nobel Prize for it in 1974. Their first commercial products were Nylon 6,6 from Carothers polyamides in 1939, Fax and Martin polyethylene in the 1940s, and Kipping organosilicium compounds in the 1950s, respectively. In the 1930s, the development of polyethylene, a plastic made from ethylene, revolutionized the polymer industry. Polyethylene is a lightweight, durable material that is resistant to water and chemicals and is ideal for use on a wide range of products including bottles, containers, and tubes. Over the years, scientists have continued to develop new types of polymers, including polypropylene, polyvinyl chloride, and nylon, which are used in a variety of applications including clothing, automotive parts, and medical devices. Today, polymers are an integral part of our daily lives and are used in a wide range of products, from packaging materials to construction materials, from medical implants to electronics. In conclusion, the history of polymers is long and varied, with advances in polymer technology having a profound impact on many aspects of our daily lives. From the early developments of Celluloid and Bakelite to the widespread use of modern synthetic polymers, these materials have played a vital role in the evolution of many industries and continue to shape the world in which humanity lives today (Farber, 1963; Morawitz, 1985).

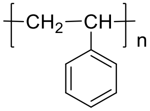
1.1.2.Polymers

The term polymer consists of the Greek roots poly (many) and meros (part). Polymers contain thousands to millions of atoms in a large molecule formed by the combination of very small molecules called monomers, which are also called macromolecules**.** One of the key characteristics of polymers is their molecular structure, which is made up of long chains of monomers linked together. The type and arrangement of these monomers can vary, leading to a wide range of physical and chemical properties in different polymers. For example, polystyrene is a synthetic polymer composed of monomers called styrene that are linked together in a chain-like structure (Young et al., 2011; Zaquen et al., 2015).

Monomer is a concept that denotes a single repeating unit (mer) and must be structurally identical to the repeating unit. As Formula I sees, the repeating unit of polystyrene is the group $CH_2CH\text{-}C_6H_5$ of the monomer styrene.



Formula I. The repeating unit of polystyrene



Formula II. “n” determines the number of repeating units in the polymer

The “n”, which represents the number of repeating units in the polymer molecule, is also shown under parentheses with a subscript in Formula II (Carraher, 2017; Morawitz, 1985).

1.2.Nomenclature of Polymers

Cem Gök, Mine Sulak, Arzum Işıtan

1.2.1.Source-based names

When naming polymers, the prefix “poly” is added to the name of the repeated monomer. For example, the polymer derived from the ethylene monomer is called poly(ethylene) (Figure 1.1).

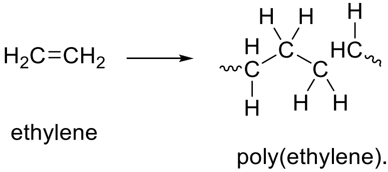


Figure 1.1. Nomenclature of poly(ethylene)

This rule applies to condensation polymers as well. In the poly(ethylene terephthalate) polymer, the ethylene part of ethylene glycol, which is one of the monomers that make up the poly(ethylene terephthalate) polymer, is taken and the terephthalate part of the second monomer, terephthalatic acid, is taken, and finally the nomenclature is completed by adding poly in front of it (Figure 1.2).

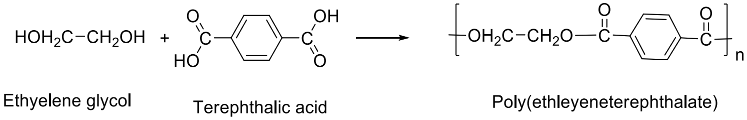


Figure 1.2. Nomenclature of poly(ethylene terephthalate)

1.2.2.Structure-based name

While source-based nomenclature is generally used for simple polymers, the International Union of Pure and Applied Chemistry (IUPAC) system is used for naming more complex polymers. With respect to IUPAC rules, the nomenclature of a polymer, the monomer units that make up the polymer chain, organic compounds that define the molecule's functional group and carbon skeleton are named according to IUPAC rules (IUPAC, 1974; Jenkins, 1998). An example of nomenclature according to IUPAC is given in Figure 1.3.

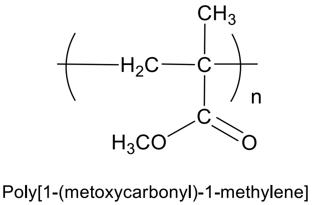
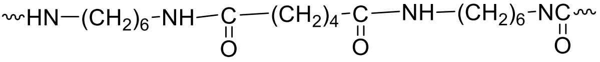


Figure 1.3. Nomenclature of poly[1-(methoxycarbonyl)-1-methylene] according to IUPAC

1.2.3.Trade names and non-names

Special terminology based on trade names is also widely used in some polymers. An example of trade name nomenclature is the use of the nylon name for polyamides derived from unbranched aliphatic monomers. When naming a polyamide, the number of carbons in the diamine and the number of carbons in the diacid are given.

For example; poly(hexamethylene adipamide), obtained from the condensation of hexamethylene diamine and adipic acid containing six carbon atoms each, is called nylon 6,6. (IUPAC, 1974; Jenkins, 1998) (Figure 1.4).



$$\sim HN-(CH_2)_6-NH-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-NH-(CH_2)_6-N\underset{\underset{O}{\|}}{C}\sim$$

Poly(hexamethylene adipamide)

(Nylon 6,6)

Figure 1.4. Nomenclature of poly(hexamethylene adipamide)

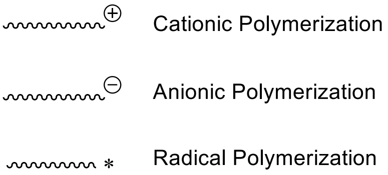
1.2.4.Degree of polymerization

Degree of polymerization is a term that indicates the number of repeating units that make up a polymer molecule. The abbreviation DP is used for the degree of polymerization. The relationship between the degree of polymerization of the same macromolecule and its molecular weight M is given as follows; M=(DP)Mo, where Mo is the formula weight of the repeating unit (Shrivastava, 2018).

1.3.Mechanism of Polymerization

Cem Gök, Mine Sulak, Arzum Işıtan

The conversion of monomer molecules into polymers is called polymerization. The methods used in the synthesis of polymers are step polymerization (condensation polymerization) and addition polymerization (chain polymerization) as divided into two. Addition polymerization is divided into two as chain polymerization (radical polymerization) and ionic chain polymerization (ionic polymerization). Ionic chain polymerization is divided into two as cationic chain polymerization (cationic polymerization) and anionic chain polymerization (anionic polymerization). In cationic polymerization, chain growth occurs through cationic centers, and in anionic polymerization, through anionic centers. Polymer chains are formed by successive incorporation of monomer molecules into active centers (Kissin, 1989).



1.3.1.Radical addition polymerization

In radical addition polymerization, the active ends of the growing polymer chains are unpaired electrons, that is, radicals. With the addition of the monomer, these radicals are transferred to the end of the chain and chain growth continues. Various radical initiators are used in radical addition polymerization.

Organic azo compounds and peroxides are among the most widely used radical initiators, and they are easily decomposed by heat to form radicals. The radical decomposition reaction for benzoyl peroxide is as follows (Odian, 2004) (Figure 1.5).

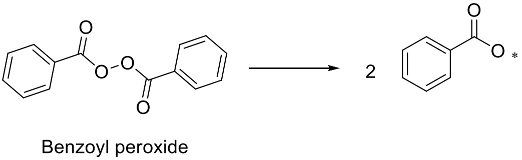


Figure 1.5. Radical formation from benzoyl peroxide for polymerization

Redox initiators such as hydrogen peroxide and persulfates can easily create radicals even at room temperature (Figure 1.6).

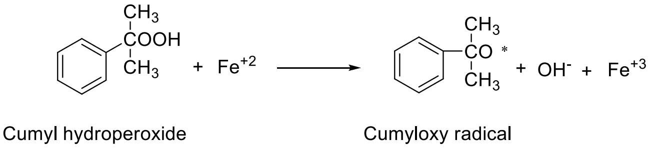


Figure 1.6. Formation of cumlyoxy radical

Free radical polymerization consists of three steps: initiation, propagation, and termination.

i) ***Initiation:*** The benzoyl peroxide decomposes to form radicals, and the initiation reaction begins with styrene, which is a monomer in the environment (Figure 1.7).

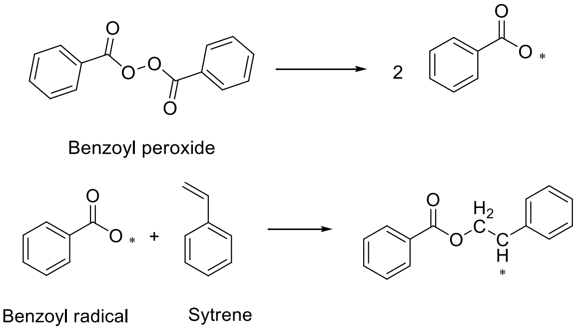


Figure 1.7. Initiation of polystyrene

ii) ***Growth:*** The growth phase proceeds by cascading monomers to the first monomeric active center formed (Figure 1.8).

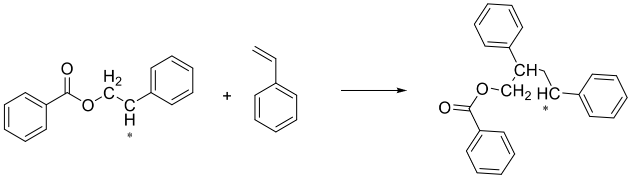


Figure 1.8. Growth of polystyrene

iii) ***Termination:*** Termination reactions are the phase of polymeric growth where chains lose their activity and turn into inactive polymer chains. Termination reactions occur in two different ways: combined termination and separate termination (Figure 1.9).

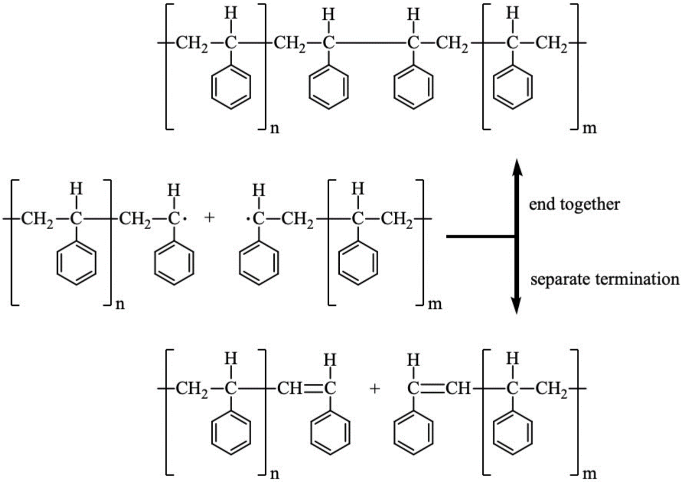


Figure 1.9. Types of termination reactions

1.3.2.Cationic polymerization

In cationic polymerization, chain growth largely depends on the structure of the ion at the end of the chain and the counter ion (Saçak, 1998; Staudinger, 1920).

i) ***Initiation:*** AICI$_3$, BF$_3$, at initiation of cationic polymerization Lewis acids such as BCl$_3$, TiCl$_4$, SnC1$_4$ and HCl, H$_2$SO$_4$, HCIO$_4$ strong protonic acids are used (Figure 1.10).

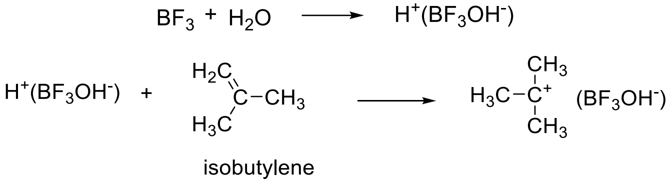


Figure 1.10. Initiation of cationic polymerization of isobutylene

ii) ***Growth:*** In the cationic polymerization of isobutylene initiated with the H$^+$ (BF$_3$OH$^-$) complex, the growth step proceeds through the following reaction (Figure 1.11).

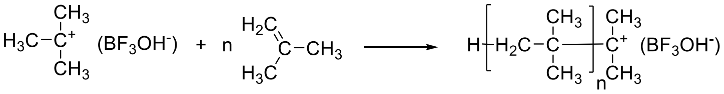


Figure 1.11. Growth of cationic polymerization of isobutylene

iii) ***Termination:*** Initiated by the H$^+$(BF$_3$OH$^-$) complex of isobutylene. In cationic polymerization, termination occurs when the catalyst complex is transferred to the monomer molecule. While an unsaturated bond is formed at the polymer end, freshly formed active center can maintain the polymerization (Figure 1.12).

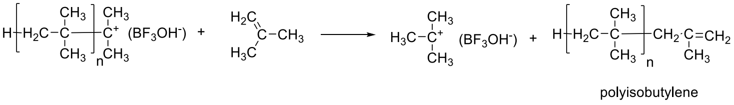


Figure 1.12. Termination of cationic polymerization of isobutylene

1.3.3.Anionic polymerization

In anionic polymerization, the initiator is the anionic end, that is, the carbanion (Saçak, 1998; Staudinger, 1920).

i) ***Initiation:*** Potassium amide (KNH_2), alkali metals, n-alkyl lithium compounds such as n-butyl lithium or Grignard compounds such as alkyl magnesium bromides can be used as initiators (Figure 1.13).

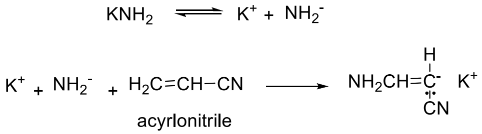


Figure 1.13. Initiation of anionic polymerization of acrylonitrile

ii) ***Growth:*** In the growth phase, as in radical and cationic polymerization, monomers join the anionic active center one after another and growth occurs (Figure 1.14).

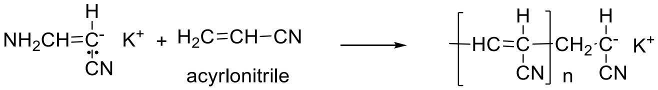


Figure 1.14. Growth of anionic polymerization of acrylonitrile

iii) ***Termination:*** Termination in most anionic polymerization systems reactions is not observed, the polymerization reaction continues until the monomer in the environment is completely consumed (Figure 1.15).

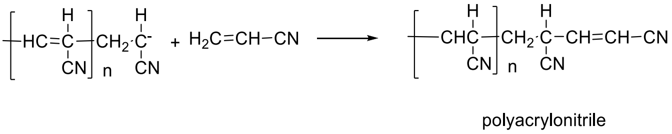


Figure 1.15. Termination of anionic polymerization of acrylonitrile

1.3.4.Step polymerization

In step polymerization, monomers, dimers, trimers etc. they can all react together. Condensation polymerization is a process in which two monomers are linked together through a chemical reaction that releases a small molecule such as water or alcohol. This type of polymerization typically requires a catalyst to accelerate the reaction. Examples of polymers formed through condensation polymerization include nylon, polyester, and polyurethane. Poly(ethylene terephthalate) polymer synthesis can be given as the most common example of step polymer (Saçak, 1998; Staudinger, 1920) (Figure 1.16).

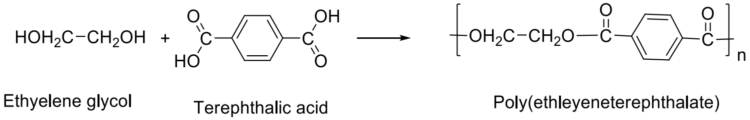


Figure 1.16. Poly(ethylene terephthalate) initiation of step polymerization

Overall, polymerization is an important process that allows the creation of polymers with a wide variety of properties and applications. Understanding the mechanisms behind polymerization is crucial for developing new polymers and optimizing their performance in a variety of applications.

1.4.Modification of Polymers

Cem Gök, Mine Sulak, Arzum Işıtan

Modification of polymers is the combination of polymerization and polycondensation in the synthesis of high molecular weight compounds. In fact, polymerization and polycondensation is a step based on the modification of the polymer, although the monomers are converted into polymers. The modification process can be chemical or physical. Chemical modification involves a series of reactions in which there is no degradation on the main chain of macromolecules, while physical modification includes both stabilizing and strengthening reactions. It is obtained by adding agents and mixing different polymers. Polymer modification is done as needed. For example, many insoluble polymers can be converted into soluble high molecular weight compounds. Polymer modification is one of the most important methods of many laboratories and industries (Korshak, 1980; Woodward, 1989).

1.4.1.Polymer modification reactions

There is no general rule in polymer modification reactions. The effect of the nature of the reagents and catalysts, the structure and crystallinity of the polymer, temperature, the nature of the solvent can be listed among the physical and chemical factors that have important effects on the course and results of the process. Due to the variables, different macromolecules are obtained with different combinations of different units.

1.4.1.1.Displacement modification

In this type of modification, different types of polymers are produced in terms of structure and properties, thanks to the interchangeable groups.

An example of this is that the new polymer obtained by replacing the hydroxyl group in the polymer with the acid or alkyl group becomes soluble in inorganic solvents.

1.4.1.2.Structure formation modification

In the modification of polymers, structure formation is a process in which macromolecules transform into branched structures and turn into soluble and insoluble three-dimensional structures. The resulting branched polymers are used in the rubber industry with their stronger, higher thermal stability and three-dimensional properties than linear polymers.

1.4.1.3.Degradation modification

Fragmentation, structure formation, reduction of the molecular weight of polymers is a process that is completely opposite to modification. Fragmentation is widely used in the processing of natural polymers such as rubber and cellulose. To obtain optimum size polymers from a macromolecule, mechanochemical and oxidative decomposition methods are used.

1.4.1.4.Participation modification

Another method used for the modification of polymers is addition reactions. If the polymers contain more than one carbon-carbon bond in the chain, halogens, oxidants, hydrogen, and other reagents can be easily added to these polymers. Polymers obtained by adding halogen to the polymer chain generally become more soluble and chemically more stable.

1.4.1.5.Elimination modification

Separation of low molecular weight substances such as water, alcohols, hydrogen and halides are one of the important polymer modifying methods. As a result of elimination, a double or triple bond, or even a ring, can form on the starting polymer, and all these reactions can be used to modify polymers.

1.4.1.6.Isomerization modification

The physical and chemical properties of the polymers obtained by the isomerization reaction are different from each other. Reactions in which the basic skeleton of the macromolecule is rearranged without any change in the basic composition of the polymer are isomerization reactions. Heating and high-pressure curing may sometimes be required in the isomerization reaction.

1.4.1.7.Change modification

In all the modification methods mentioned earlier, new polymers were formed without changing the structure of the first polymer chain. This modification method, based on the use of exchange reactions between macromolecules, leads to the formation of a polymer containing the initial polymer units in the chain. As a result, copolymerization is carried out by this method (Figure 1.17).

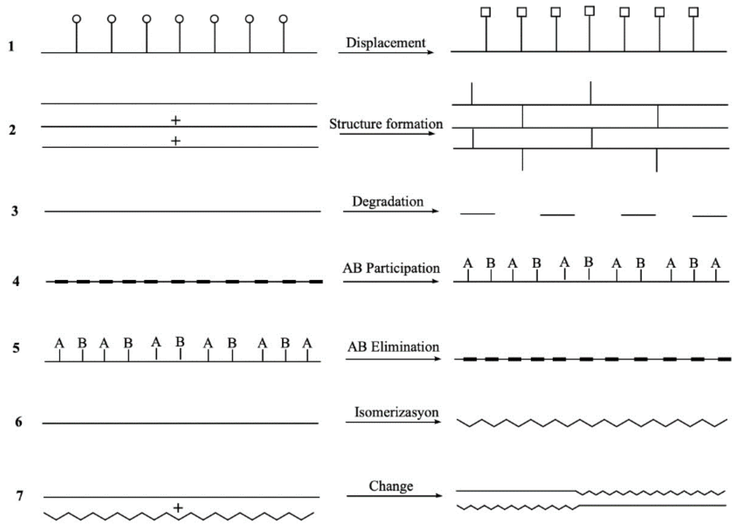


Figure 1.17. Change in the structure of modification polymers

1.5.Types of Polymers

Cem Gök, Volkan Onar, Arzum Işıtan

The rapid spread of polymers is due to the fact that their properties show many differences. Flexibility, strength, toughness, and transparency can be found in different components with different properties. Sometimes more than one feature can be provided in a single structure. Custom-made polymers can be obtained by connecting different monomers with different bonds. When the monomer number is too high, the product is called as a high polymer. In living things, it is found in different proportions as polymers, proteins, cellulose, and nucleic acids. However, quartz can be found in minerals such as feldspar and diamond, while it is also found in man-made materials such as synthetic rubber, glass, plastic, concrete, and paper.

Polymers are divided into three according to their commercial availability. They are natural, synthetic, and semi-synthetic polymers.

i) Natural polymers, such as rubber, cellulose, starch, and protein, are among the polymers found naturally in animals and plants.

ii) Synthetic polymers are polymers that are not found in nature but are produced. The most common polymer types are synthetic polymers. The most well-known of these polymers is Nylon-6. Nylon-6 is frequently used in dairy products and various industries.

iii) Semi-synthetic polymers are polymers obtained after chemical modification of natural polymers found in nature. Examples of these are the cellulose groups that come to mind first.

Polymers, natural and synthetic according to their origin and sources, amorphous and crystalline according to their chemical structure, inorganic, organic polymers, homopolymer, heteropolymer and copolymers according to their structure, linear polymers, branched polymers, cross-linked polymers, graft polymers, block polymers according to their structure. Polymers can be classified in many ways, such as thermoplastics and thermosets based on their thermal characteristics, and according to the type of polymerization, including addition, copolymerization, and condensation polymerization. Additionally, polymers can be classified in various ways based on their application and end use, including tactics such as Isotactic, Syndiotactic, and Atactic. The polymer types are presented under certain headings below given in Figure 1.18 (Campbell et al., 2000; Ehrenstein, 2001; Nicholson, 2006; Singh and Dubey, 2009; Gupta, 2010; Gad, 2014).

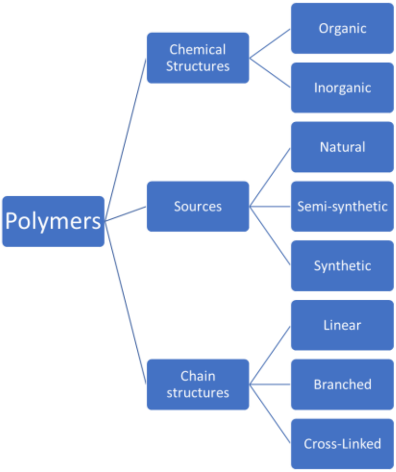


Figure 1.18. Polymer classification

1.5.1.Chemical structures

1.5.1.1.Organic polymers

The polymers that form the basic structure of living organisms and provide lifelong support to the organism, in which the backbone chains consist of carbon atoms, are called organic polymers. Organic polymers can form the main structure of all plants such as, cellulose and resins. Proteins and rubber are other organic polymers (Klemm et al., 2005; Yu and Chen, 2009; Ozcan et al., 2013; Silvetti et al., 2017; El Knidri et al., 2020).

1.5.1.2.Inorganic polymers

Inorganic polymers are also known as polymers. These polymers are macromolecules whose backbones consist of chains of elements other than C. When their chemical structures are examined, it is seen that they are alkali aluminosilicates. Structurally, they are aluminosilicates composed of Si and Al tetrahedra bonded by repeated oxygen atoms. Inorganic polymers are increasingly used in many industrial applications thanks to their low CO_2 emission, easy production and applicability, good mechanical properties, high corrosiveness, and fire resistance. In addition to these important features of inorganic polymers, the biggest disadvantage is their brittleness. Examples of inorganic polymers are macromolecules such as polysilanes (Si-Si), polysilazanes (Si-N), polysiloxanes (Si-O or silicones) (Korniejenko et al., 2018).

1.5.2.Sources

1.5.2.1.Natural polymers

Natural polymers are responsible for performing various basic functions of living things. Proteins and polysaccharides undertake these basic functions (Arar et al., 2022). Some natural polymers, such as cellulose rubber and chitin, ensure the cellular integrity of plants and animals, while others provide protection against the external environment. Therefore, natural polymers can be obtained from a wide variety of sources, from plants (resin, cellulose) to animals and microorganisms (Solmaz et al., 2018). Resins are polymers of simple hydrocarbon isoprene like rubber. Cellulose is a polysaccharide polymer composed of sugar molecules.

1.5.2.2.Semi-synthetic

Semi-synthetic polymers are polymers obtained by chemical reaction from natural polymers that can be found in nature. Cellulose acetate and cellulose nitrate are examples of this group of polymers.

1.5.2.3.Synthetic

This group of polymers can be produced by many different processes. Conversion into polymers can be achieved by adding monomers to simple hydrocarbon chains one by one. An example of synthetic polymers is polyethylene. It is formed by the combination of ethylene monomers. These monomers can be formed by linking together 10000 monomers in long helix (Gad, 2014; Harrats et al., 2016; Rial, 2022).

1.5.3.Chain structures

1.5.3.1.Linear

This polymer group is a long and continuous carbon-carbon chain in which two of the vacant valence electrons are attached to hydrogen or hydrocarbon (Gao, 2021).

1.5.3.2.Branched

This polymer group has side chains growing from the backbone. Side chains are identical to the main polymer chain and consist of repeating units. Increased branching (side chains) causes a decrease in the crystallinity of the polymer. The most well-known branched polymer is polyethylene with low density.

1.5.3.3.Cross-linked

This group of polymers has a wide variety of properties that increase its use. It is the formation of covalent bonds in which several polymer chains different from other polymer groups are brought together. This phenomenon is called as cross-linking. It changes the chain structures that facilitate phase transitions by allowing the ingress of water or organic solvent into the 3D polymer networks created through cross-linking. This causes changes in properties such as swelling, transparency and flexibility. The change in the amount of crosslink in the structure also allows the swelling property to differ. They show higher mechanical properties than other polymers. The most commonly used cross-linked polymers in our environment are plastic pottery and epoxy resin adhesives (Saldívar-Guerra and Vivaldo-Limo, 2013).

1.6.Application of Polymers

Cem Gök, Volkan Onar, Arzum Işıtan

Today, polymer materials are used in a wide variety of fields. At the forefront of these are various fields such as the food and packaging industry, the automotive industry, the textile industry, the aviation industry, electronic applications, the pharmaceutical industry, optic sport, cosmetic, biomedical engineering, and the construction industry (Özcan et al., 2015).

i) ***Automotive industry:*** In line with the demands of automobile users to lead a comfortable life, the automotive industry has also started to search for different materials. However, due to low exhaust emissions and desired fuel economy, the use of lightweight, high-performance advanced polymers has increased in the automotive industry. Today, polymers with good corrosion resistance, flexibility, strength, and low cost are used in the automotive industry. PP is one of the leading polymers used, and it is widely used in vehicle bumpers (Cheremisinoff, 1991).

ii) ***Aviation industry:*** The development of modern aviation necessitates the use of various materials. The materials used in the aviation industry must be easily shaped and possess high strength and lightness. This requirement is met using polymer materials. Instead of using polymers alone, the preference has been for the use of polymer matrix composites. The most used composite materials include resins and polyesters derived from polymer materials (Kesarwani, 2017; Parveez et al., 2022).

iii) ***Packaging industry:*** This sector is used in various industries, especially in the food sector, pharmaceuticals, medicine, electronic devices, and many others, thanks to its applications in different fields (Tajeddin and Arabkhedri, 2020; Siva et al., 2023).

iv) ***Textile industry:*** In order to meet the increasing demands of humanity day by day, the textile sector continues to experience innovations. The use of polymers has increased in various areas within the textile sector. Polymers are the primary materials in the textile industry. While polymers are used in the production of dyes and sizing in the sector, today, they have also started to be used in the production of intelligent textile materials. The most used polymers are cellulose and cotton (Hu and Chena, 2010; Hu and Lu, 2012).

v) ***Electronic applications:*** With the development of technology, the use of polymer materials in electrical and electronic equipment has increased. Polymers are used in the manufacture of chips, electrical circuits, device enclosures and for insulation purposes. Its features such as being recyclable, having low density, being flexible, being easily shaped and having low production costs are among the reasons for preference. Today, their use is increasing in many electronic systems such as external memories, diodes, capacitors, indicators, sensors, smart devices (Wei et al., 2018; Bhadra et al., 2019).

vi) ***Biomedical engineering:*** Today, it is seen that researches are carried out in line with the needs in the field of health and new biomaterials are developed. There have been great developments with this biopolymer, which has started to be used in the field of health. Polymeric biomaterials are the most important materials used in healthcare applications. These developments continue with both direct intervention to the tumor by drug release and the use of biopolymer materials produced in prostheses and organs (Myung et al., 2011; Deng et al., 2012; Tüylek, 2019; Gönenmiş and Özcan, 2022).

vii) ***Food industry:*** Edible polymers used in the food industry constitute basic foods. These polymers react with each other to form foods with better properties. Edible polymers are examined in 3 groups. These are proteins and polysaccharides, lipids, and composites, respectively. Today, cellulose, whey, gelatin, chitosan, collagen, alginate, and starch are among the most used edible polymers. In addition, these polymers that mentioned are not only used to be eaten but also used to improve the quality of life of people with certain diseases (celiac, lactose sensitivity, diabetes, etc.) (Gutiérrez, 2018).

viii) ***Construction industry:*** Polymers are at the forefront of the materials that have been used as building materials in recent years. In the past, wood was used as a support material and straw as a covering material in the construction of shelters and houses, but today it is used in the construction of lighter structures and objects due to its lightness, in molding and shaping due to its good formability and in facade cladding and paints due to its good chemical resistance.

Since it is suitable for recycling, it has started to be used in every part of the buildings built in the last 20-30 years and its use is increasing day by day (Correia Diogo, 2014).

1.7.Biopolymeric Materials

Cem Gök, Arzum Işıtan

Biopolymers are polymeric materials produced from natural sources either chemically synthesized from a biological material or entirely biosynthesized by living organisms such as cellulose and starch, proteins, peptides, and DNA (Gok and Aytas, 2014; Smith et al., 2016). Due to their unique characteristics, they have recently attracted a lot of interest from the scientific community. These biopolymers consist of long chain-like molecules containing repeating monomer units, like conventional polymers, derived from living organisms, such as plants and microbes, rather than from petroleum, the traditional source of polymers (Mohiuddin et al., 2017).

The majority of biopolymers are biodegradable into the environment and display non-toxicity. The use of biopolymers is expanding steadily today across a variety of industries. It is because of their distinctive qualities, including renewability, compatibility with the environment, antibacterial action, biocompatibility, and biodegradability (Niaounakis, 2013; Swain et al., 2018).

The primary characteristic that sets biopolymers apart from polymers obtained from fossil fuels is their sustainability, particularly when paired with biodegradability. Biodegradable biopolymers have been synthesized from renewable resources to replace polymers derived from fossil fuels (Mohan et al., 2016). Biopolymers, consisting of molecules with linear or branched/cross-linked chain-like structures, could be the way to revolutionize the material world. Most biopolymers' monomer units are typically made up of repeating molecules of either nucleic acids from nucleotides, amino acids from proteins, or saccharides made from sugars. The monomeric units are grouped locally within their basic structures to generate secondary structures, and occasionally they even take on the profile of a three-dimensional framework to form a tertiary structure (George et al., 2020).

Biopolymers typically have a structure made up of monomeric units that are covalently connected to one another. Like synthetic polymers, biopolymers can have different structural arrangements. Basic topologies for polysaccharide-based biopolymers include branching and linearly linked monosaccharide units. In contrast, only the linear form predominates in biopolymers based on proteins and nucleic acids. Helical pleated or three-dimensional coiled structures have been seen in the secondary or tertiary architectures of biopolymers (Yaashikaa et al., 2022).

To gain a vivid grasp of the chemistry associated with biopolymers, it's worth noting that biopolymers, categorized by their derived source, produce certain types of chemical reactions. The natural type may include starch that has coalesced with esters, chitosan-cellulose, or even particular alcohols (George et al., 2020). There are four main categories of biopolymers, each based on one of the following: starch, sugar, cellulose, or synthetic ingredients.

The starch-based polymer is a naturally occurring polymer that appears as granules in plant tissue and may be readily extracted in significant amounts. It is derived from sources like potatoes, maize, wheat, tapioca, and others. It is possible to modify starch to be thermoplastically melted and reconfigured. Hence, the final product is appropriate for common plastic-forming procedures like injection molding and extrusion (Gok and Aytas, 2014). Figure 1.19 depicts the chemical compositions of some biopolymers used in commerce.

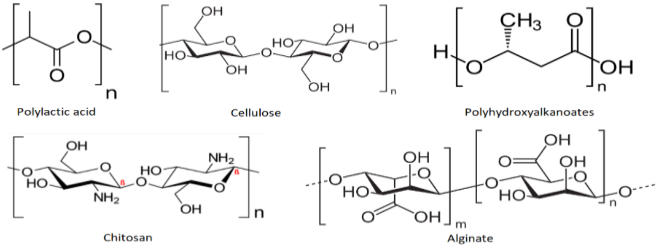


Figure 1.19. Chemical structures of some commercial biopolymers (George et al., 2020).

Many research areas have focused on biopolymers due to their biodegradability and biocompatibility. These characteristics of biopolymers have led to extensive research into their potential for use in many different treatment applications in comparison to more traditional materials. Sustainability and green technology are becoming increasingly significant in today’s world. By lowering reliance on non-renewable fossil fuel raw materials, the introduction and development of biopolymers offer a path to achieving a sustainable environment (Subash et al., 2023).

It is typical for biopolymers to have properties that fall into three main categories. Relative properties, which refer to the characteristics of the polymer as a whole; synthesizing properties, which describe the behaviors during formation; and component properties, which refer to the polymer’s functional capabilities. Each of the properties of these three classes interacts with the others to create the desired entity (George et al., 2020).

A polymer’s basic and innate qualities can exhibit a wide range of relative properties depending on its structure and/or chemical composition. The performance and functionality of biopolymers are influenced by relative biopolymer qualities such as density, crystallinity, permeability, and transparency. The qualities gained during the production phase are called “synthesis properties”. They consist of various details such as viscosity, thermal deformation temperature and stability, melt flow index, wettability, and many other mechanically related properties that are important during the production stage. Any polymer’s component properties are the ultimate result of a crucial fusion of relative and synthesizing qualities that give rise to certain distinguishing characteristics. Biopolymer component properties influencing performance and usefulness include the polymer’s wearing resistance, impact and static modifiers, and aesthetic properties (George et al., 2020).

The tendency of biopolymers to degrade rapidly at high temperatures is one of their main disadvantages. The major disadvantage of not having adequate heat resistance is typically determined by the heat deformation temperature. Several techniques, such as random and block copolymerization or grafting, have been developed to improve the properties of biodegradable polymers. These techniques increase the finished goods' mechanical qualities as well as their rate of biodegradation. Another method for creating biodegradable materials with various morphologies and physical properties is physical blending.

However, it is known that the strength, stability, and other mechanical qualities of biopolymers are inferior to synthetic ones in various manufacturing industries. A proposed strategy is given to improve the quality and importance of biopolymers by integrating the reinforcing agent into the micro/nano regime of the polymer matrix to counteract this loss of functionality while preserving an eco-friendly garment. As a result, a petroleum-based competitor was created using biopolymer composites (Gok and Aytas, 2013; Gök, 2017; Özcan et al., 2022).

Moreover, crosslinkers are unique bifunctional compounds that bind molecules together and increase the molecular weight fraction of finished products. The finished biopolymer web can be more stable and have improved mechanical properties as a result. Different types of crosslinkers, including glutaraldehyde, epichlorohydrin, glyoxal, formaldehyde, divalent cations, ethylene glycol diglycidyl ether, isocyanates, genipin, and triphosphate, have been studied in addition to various crosslinking techniques, such as chemical, physical, thermal, and enzymatic crosslinking (Gok et al., 2013; Aytas et al., 2016; Özdil and Özcan, 2023). As a result, biopolymers' qualities will improve, and they will become more competitive with traditional polymers.

Biopolymers are sustainable material and have a number of positive economic and environmental effects. Moreover, biopolymers might be useful for the treatment of garbage. For instance, using biopolymers instead of polyethylene to make coated sheets could help reduce plastic waste in compost. It is necessary to compare the life cycle analysis of each application with existing methods to determine whether the use of biopolymers will result in a more sustainable society. Representative lifecycle studies are needed at the material and product level. They must consider all relevant environmental impacts associated with the entire product life cycle, including depletion of raw materials, agricultural use of fertilizers and pesticides, transportation, use and disposal, as well as future advances in biopolymers (Gok and Aytas, 2014; Işıtan et al., 2022).

PLA, alginate, chitosan, cellulose esters, gums, starch plastic, carrageenan, silk and aliphatic polyester-copolyesters are all biodegradable polymers. When biopolymers were first commercialized, emphasis was placed on short-term uses; however, current research and development aims to increase the durability of these polymers. To create higher quality polymers, researchers began using genetically modified crops. However, the biggest problem with biopolymers remains their relatively expensive cost (Christian, 2016; Khademian et al., 2020).

Due to its potential uses in the sectors of environmental preservation and the maintenance of physical health, biodegradable polymers have drawn a lot of interest in recent years. Only a few of the mentioned biopolymer groups are currently significant on the market. Their price level, which is now uncompetitive, is the key factor. The future of each biopolymer depends not only on how competitive it is, but also on how willing society is to pay for it. Prospects for progress in the field of biopolymer materials are encouraging.

1.8.Preparation of Biopolymers

Cem Gök, Arzum Işıtan

A suitable feedstock for the synthesis of biopolymers includes a variety of natural sources, including plants, animals, agricultural waste, and microorganisms. Corn stalks, maize, wheat, potatoes, and barley are a few examples of agricultural or plant-based supplies. Biopolymers are made from biomass sources such as crops and green waste. Recently, it has been observed that industrial waste residues are used as a source of biopolymers. Studies on biopolymers have also been carried out on marine creatures including lobster, fish, and shrimp. Similarly, microbially derived biopolymers have become more significant in recent years. Vegetable oils such as sunflower, rapeseed, corn, castor, and linseed oils are also used in the synthesis of biopolymers. (Yaashikaa et al., 2022).

Depending on their raw material source, biopolymers can also be divided into natural, microbial and synthetic categories. Natural biopolymers mainly derived from biomass can be divided into two groups: those based on proteins, such as gelatin, gluten, soy protein, albumin, elastin, fibrin, alginates, microfibrillar, collagen, and keratin, and those based on polysaccharides, such as those derived from cellulose, starch, algae, chitosan, and many others. Synthetic polymers are man-made molecules and, unlike natural polymers, they do not occur naturally. Biosynthesized polymers are ideal for a variety of applications, including agro-industrial, agricultural, medical, environmental, and packaging applications. These polymers include capsular and exopolysaccharides, including pullulan, bacterial cellulose, xanthan, microbial polysaccharides, and dextran. The most used synthetic biopolymers are those produced synthetically or chemically. They include systems like polylactic acid (PLA) and petroleum-based goods like poly-caprolactone (PCL), polyhydroxy alkenoates (PHA), xanthan, gellan, and dextran (Chaabouni et al., 2013; Subash et al., 2023).

Biopolymers can be produced in a variety of methods to suit a variety of uses. Many biopolymers are derived from plants and algae that develop in natural habitats and are found in abundance there. Agar and alginates are obtained from different types of brown algae, commonly known as seaweeds, or from red algae of the species of Gelidium. Very few biopolymers are separated from incredibly natural sources. Hyaluronic acid taken from the umbilical cord of newborns is an example of an exception to this rule. Another way to make biopolymers is by in vitro synthesis using isolated enzymes in cell-free environments. An example of this is the use of heat-stable DNA polymerases in the polymerase chain reaction (PCR) to create monodisperse and well-defined DNA molecules. Dextran is another example; it can be produced on a large scale using isolated dextran sucrase. Biopolymers produced by fermentation, such as polysaccharides, are used in industry. Biopolymer formation in biotechnology can occur either intracellularly or extracellularly. This has a number of serious implications regarding the constraints on upstream and downstream processes to produce biopolymers in their pure state (Rao et al., 2014).

The most prevalent natural polymer obtained from wood sources is cellulose, which is made up of β-D-glucopyranose units joined together by a β-1,4-glycosidic bond. The molecular structure of cellulose affects properties including chirality, hydrophobicity or hydrophilicity, and degradability (Subash et al., 2023). A very pure cellulose product with different qualities, in addition to being traditionally obtained from plant tissue (wood, cotton, etc.), can also be formed by fermentation by some types of bacteria (Rao et al., 2014).

The linear copolymer alginate, which contains the mannuronic acid (M) and guluronic acid (G) subunits, is widely produced by brown algae and some bacteria. Alginate has been utilized extensively in water purification applications due to its biocompatibility, biodegradability, lack of toxicity, and inexpensive cost compared to other biopolymer materials (Gok et al., 2013). The algae are treated with a base solution to release the alginate. Alginic acid is the product of its interaction with acid. Alginate is a binary copolymer with no branches. Depending on the sources, the ratio between the two monomers varies. In the presence of counterions, such as divalent cations like Ca^{2+}, alginic acid can produce gels. The degree of crosslinking in this polymer depends on the pH, the type of counterion, and the functional charge density. Gelling ability allows encapsulation of different components (Vroman and Tighzert, 2009).

Alginate is a naturally occurring polymer that can be cross-linked with divalent calcium ions to create hydrogels. Because of its benefits, which include biodegradability, hydrophilicity, the presence of carboxylic groups, and natural origin, it has been chosen over other materials. Alginate is a good example of a material that may simply undergo a polymerization process to transform into a biopolymer. A 0.5 or 1 mol/L $CaCl_2$ solution can be made into calcium alginate beads by adding dropwise a 1% to 4% viscous sodium alginate solution while keeping the temperature at around 4°C. After stirring for one hour, the gel beads are collected and kept in a $CaCl_2$ solution at room temperature. Cross-linked Ca-alginate is created when Na-alginate interacts with $CaCl_2$ to create beads. Alginate gels take on the cross-linked chain structure known as the “egg box” pattern when calcium or other divalent cations are present. Alginate can be converted into a hydrogel by cross-linking with divalent calcium ions in an “egg-box” model in which both divalent and polyvalent metal ions are bonded to two carboxyl groups as adjacent alginate molecules. Water-soluble sodium alginate is converted into water-insoluble calcium alginate beads during the procedure. After washing with deionized water to remove $CaCl_2$ from the bead surfaces, the obtained beads are kept waiting. Filtration is used to collect the beads, and the filter paper is used to absorb any extra water. The beads are then allowed to dry at room temperature or in an oven set to about 50°C (Gok, 2010). Some photos from the preparation stages of alginate biopolymers are given in Figure 1.20.

Figure 1.20. Photographs of various preparation stages of alginate biopolymers

The physical or chemical modification of biopolymers is acknowledged as an essential method for altering their physical and chemical properties, producing novel materials with enhanced properties, and enabling them to be fully explored in a variety of application areas, including tissue engineering, food industries, drug delivery, separation and purification methods, biomedical, agriculture, and other industrial applications.

The drawbacks of the biopolymers can be fixed using chemical techniques. Nevertheless, physical procedures can also aid to improve the performance of biopolymers. To increase both features of the biopolymer in practice, raw biopolymers must often undergo chemical or physical modification. Modifications are sought for surface area, porosity, pore size, and other physical and chemical properties. Aside from coating, grafting, crosslinking, and combining with other polymers, there are several methods for altering biopolymers (Khademian et al., 2020).

For example, the limited use of chitin and chitosan is a result of their insoluble nature in most solvents. It is a kind of biopolymer that is used in numerous industries, including wound care and cosmetics. As chitosan contains reactive amino and hydroxyl groups, chemicals substances can be added. N-carboxymethyl chitosan and N-carboxyethyl chitosan are two ways in which modified chitosan can be made. The chemical changes of this biopolymer are interesting. These changes preserve the physical, chemical and biological capabilities of polymers without changing their basic structure. New properties can be introduced, depending on the chemical structure of the desired functional group. It is possible to prepare chitosan biopolymers in many different derivatives (Vroman and Tighzert, 2009; Özcan et al., 2022).

As people's awareness of sustainable development increases, researchers are considering using natural and biodegradable polymers to replace synthetic polymers for various uses. The physicochemical properties of materials are changed through modification, especially at the molecular scale. Future research seems likely to focus more on how modification processes affect biopolymers. These biopolymers' mechanical and barrier properties will also be improved by the addition of diverse nanofillers, which will enhance their range of applications. These materials are used more frequently in daily applications due to their biocompatibility and biodegradability. It is predicted that sustainable biopolymers will replace a sizeable portion of the market for synthetic polymers due to rising environmental awareness and the depletion of fossil fuel resources. We may anticipate a sharp increase in bioplastic-based high-value products and technologies produced specifically for the target market in the upcoming years. In any industrial manufacturing process, cost is a crucial factor. Analysis of the economy is critical to the recycling process. As a result, more research on new raw materials, improvement of the use of existing biopolymers and development of low-cost production techniques for this field are required. Biopolymers are a valid option in many applications due to their biodegradability, non-toxicity, economic sustainability, as well as their renewable, environmentally friendly, lightweight, easy to produce properties.

Highlights

- Revolutionary developments such as the discovery of polyethylene in the 1930s transformed the polymer industry and shaped modern life.
- There are various polymerization methods, including step polymerization (condensation), radical addition polymerization, cationic polymerization, and anionic polymerization.
- There are chemical and physical ways to change polymer properties with variables such as reagents, catalysts, temperature, and solvents.
- Isomerization, elimination, exchange, and incorporation modifications enrich the understanding of the complex reactions that can alter polymers while retaining their essential composition.
- We see the extraordinary impact of polymers in our daily modern life in a wide variety of sectors such as packaging, textiles, electronics, biomedical and aerospace.
- Biopolymers derived from natural sources and biosynthesized by living organisms have received great attention due to their biodegradability, non-toxicity, and renewable nature.
- Biopolymers are the materials of the future with their biodegradability, biocompatibility, and renewability properties.
- A wide range of materials, including agricultural sources, industrial waste, and marine organisms, contribute to diverse biopolymer synthesis.

Interesting questions

- What are the general structural and chemical characteristics of polymer molecules?
- How many types of methods are used in polymer synthesis?
- What are the modification types of polymers?
- Can you classify polymers according to their commercial availability?
- What are the general application areas of polymers?
- What are the main features that distinguish biopolymeric materials from other material groups?
- How are biopolymers obtained from which raw materials?

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CHAPTER 2: INDISPENSABLE POLYMERS OF LIFE: PLASTICS

Evren Çağlarer, Charlotte Thiel

2.1.Introduction

Evren Çağlarer

For millions of years and until the end of the 19th century, the substances used by human beings came from nature. With the increase in population, most of the natural resources started to become very expensive.

Mankind has worked hard to develop materials that will provide benefits not found in natural products since the earliest times. The development of plastic materials started with the use of natural materials (such as gum, shellac) with the properties of plastic, and then continued with the development of chemically modified natural materials (such as rubber, nitrocellulose, collagen, galalite). Finally, 100 years ago, completely synthetic materials, which we know as modern plastics, began to be developed. This development played a major role in protecting natural resources that are dwindling or that cannot be replenished fast enough. Initially, the quality of the synthesized plastics was relatively inferior to the material for which it was substituted. However, the ability of plastics to be molded, colored, and brought to the hardness they offer has given them an advantage (Yaşar, 2001).

2.2.Polymeric Structures of Plastics

Evren Çağlarer

Every production requires a raw material borrowed from nature, and the synthesis of plastics follows this rule. Extracts cellulose from cotton and wood from the plant kingdom and all cellulosic products from cellulose. Castor oil is the raw material of Rilsan©, that is, polyamide. Galalite, which has been used in button production for a long time, is obtained from the casein in milk, that is, from the animal kingdom. However, the main materials used in the production of plastics are mostly minerals. These can be listed as coal, oil, natural gas. No matter what realm it comes from, plastic materials are generally made up of carbon, hydrogen, oxygen and nitrogen atoms. These elements, symbolized by the letters C, H, O, N, are the human body and are the elements that compose all living things. On substances that are closer to us than glass and metals, chemists have studied how these substances arrange their atoms. As a result of this work, the concept of macromolecules emerged (Savaşçı et al., 2002). Macromolecules are giant structures containing thousands of atoms chained together. Initially, chemical manufacturers supplied plastics manufacturers with “bricks”, or monomers, to “construct” the polymer (from ancient Greek; poly = many and meros = division). Monomer represents a simple molecule consisting of chains of up to 12 atoms. The polymer is built from these monomers in two ways; polymerization and condensation polymerization.

The polymerization is made from double-bonded monomers, quickly and without by-products. Copolymerization occurs when more than one type of monomer is used. Condensation polymerization consists of molecules containing different functional groups slowly. As these groups react with each other, by-products are formed along with water, carbon dioxide and ammonia. If no by-product is formed, this addition is called polymerization.

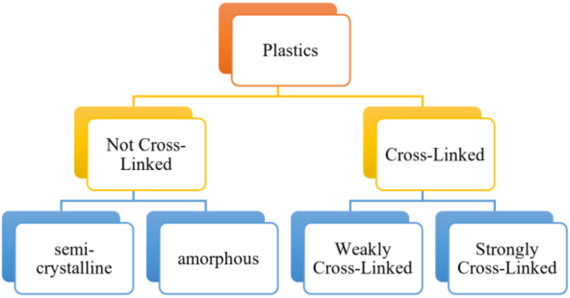


Figure 2.1. Classification of plastics

Plastics can be classified according to various criteria. They are generally divided into cross-linked and non-cross-linked plastics according to their chemical bond structure (Figure 2.1). Thermosets and elastomers are crosslinked. Thermoplastics are not cross-linked.

There are two common categories of plastic materials: thermoplastics and thermosets. Thermoplastics have a densely linear macromolecular structure. Heat pulps them, while their formal structure stabilizes when cooled. This process is reversible. That is, when they are heated again, they soften again and lose their shape. This is why thermoplastics can be transformed and used over and over again. Thanks to the 3D-like bond structures of thermoplastics, the shape of the product is fixed with heat and the bonds are strengthened and the product takes its desired shape (Savaşçı et al., 2002).

In general, the physical properties of a plastic are related to the density and arrangement of molecular groupings. The longer the chains and the more connection points, the more durable the material. The more linear and denser the chains are, the harder the material is. For example, high-density polyethylene (HDPE) is rigid because of the dense bonds, while low-density polyethylene (LDPE) is less dense, more flexible and branched. The stronger the chain structures, the stronger, more stable and temperature resistant the material is. (Figure 2.2).

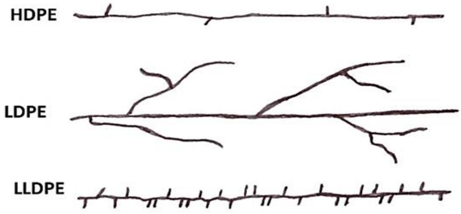
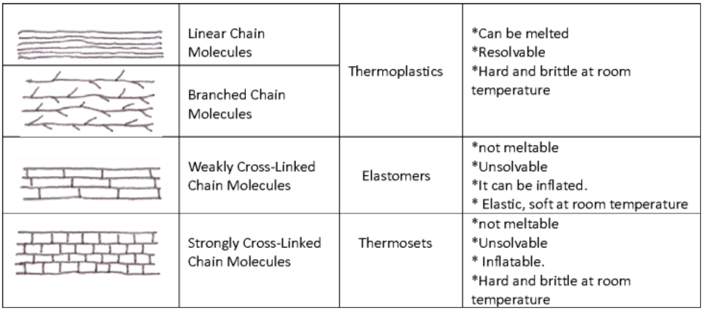


Figure 2.2. Molecular structures of different types of Polyethylene (PE)

The plastics are composed of linear or branched giant molecules, i.e., macromolecules (Figure 2.3).

There are no chemical bonds between macromolecules in thermoplastics. For this reason, thermoplastics can be reused after processing. However, thermoplastics have a disadvantage. Thermoplastics are chemically soluble (Savaşçı et al., 2002).



	Linear Chain Molecules	Thermoplastics	*Can be melted *Resolvable *Hard and brittle at room temperature
	Branched Chain Molecules		
	Weakly Cross-Linked Chain Molecules	Elastomers	*not meltable *Unsolvable *It can be inflated. * Elastic, soft at room temperature
	Strongly Cross-Linked Chain Molecules	Thermosets	*not meltable *Unsolvable * Inflatable. *Hard and brittle at room temperature

Figure 2.3. The arrangement of plastic molecules

After this, we can separate thermoplastics according to the macromolecule arrangement (Figure 2.4.). In case the arrangement of macromolecules is random, the material is called **“amorphous”**. Amorphous materials appear transparent if no additive is added to them. The plastics with molecules arranged uniformly in some regions are called **“semi-crystalline”** plastics. These do not appear transparent.

According to the production parameters, that is, depending on the environmental conditions, plastics can be produced with both amorphous and semi-crystalline properties. These plastics, however, differ from each other in terms of their working conditions and performance characteristics.

In Plastics, complete crystallization is not possible because the macromolecules are entangled with each other. In other words, there are amorphous regions between the crystallized regions in plastic materials. Plastics, the ratio of crystallized regions to the entire area is called **“the degree of crystallinity”** and this ratio may change due to operating conditions (Savaşçı et al., 2002).

But the degree of crystallinity depends more on the material itself. Materials with a simpler chain molecular structure have a higher degree of crystallinity (Figure 2.4).

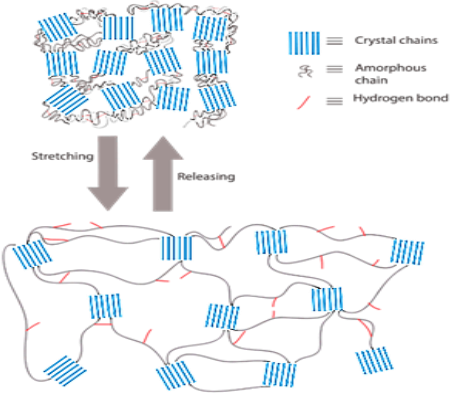


Figure 2.4. Molecular structures of amorphous and semi-crystalline thermoplastics (https://commons.wikimedia.org/wiki/File:A_stretchable_and_self-healing_seminconducting_polymer-based_material.svg)

Cross-linked plastics, which are another group other than thermoplastics, can be divided into two as weakly and strongly cross-linked plastics. Cross-linked plastics, unlike thermoplastics, cannot be reused many times. The reason why these materials are called cross-linked is that chemical bonding has occurred between macromolecules as a result of chemical reactions (Savaşçı et al., 2002).

Weak cross-linked materials are called **elastomers**. They do not dissolve with solvents but swell chemically. As the number of cross-links between macromolecules increases, the material becomes harder and more brittle, and the swelling property decreases. Materials that are strongly cross-linked in this way are called **thermosets**. They have a highly complex cross-linked structure in which macromolecules combine to form a single molecule.

2.3.Types of Plastic

Evren Çağlarer

2.3.1.Thermoplastics and some types of thermoplastics

Thermoplastics can be repeatedly moulded into any desired shape by successive heating and cooling processes and appropriate processing techniques. When the material is put into a mould in the desired shape and the material is cooled again, it returns to its old hard state. Used thermoplastics can be recycled and re-produced by applying heat and pressure. This cycle of thermoplastics usually does not change the chemical properties of the polymer too much. Theoretically, there is no limitation in repeating this process.

Thermoplastics are generally used between the glass transition temperature (T_g, the temperature at which the non-crystalline regions become less solid and elastic than the brittle and glassy state) and the melting temperature (T_m, the melting temperature of the crystalline regions), which are specific temperatures for each type. Because between these two temperatures, they are neither brittle nor fully liquid. They are located between these two states in terms of properties, so that the most suitable range is found to obtain the product in the desired shape with different processing techniques (Kıralp et al., 2007).

2.3.1.1.Polyethylene (PE)

Ethylene molecules, one of the most important petroleum chemicals, can be polymerized by adding to each other with various techniques and as a result, a wide variety of products can be obtained from low molecular weight waxes to crystalline high-density polyethylene with very high molecular weight.

Its first synthesis was realized by chance in 1898 by the German chemist Hans Von Pechmann. Its industrially applicable synthesis was carried out in 1933 by Reginald Gibson and Eric Fawcett working at the British industrial giant Imperial Chemical Industry (ICI). This material was developed in two different forms, low density, and high-density polyethylene. Today, a wide variety of polyethylene can be produced with new techniques (https://en.wikipedia.org/wiki/Polyethylene).

Low density polyethylenes are flexible, semi-light permeable, waxy, resistant to low temperatures and inexpensive. They are generally used in the production of gas and water pipes, plastic bags and other packaging products (especially packaging of food products) and a wide variety of sample and storage containers (Kıralp et al., 2007).

High density polyethylenes, on the other hand, are semi-rigid, semi-light permeable, high strength, chemical resistant, low water absorbency and at the same time inexpensive. They are generally used in the production of kitchen appliances, food coating materials, petrol tanks, milk, and liquid detergent containers (Kıralp et al., 2007).

2.3.1.2.Polypropylene (PP)

It is produced by polymerization of propylene gas. Polypropylene is also a by-product of oil refining.

The invention of Polyethylene led to the invention of a more advanced material, Polypropylene, in the early 1950s after World War II. In modern science and technology, it is a common situation that inventions made in different places at the same time are the same. For propylene, it can be said that this event is at a very extreme point. Because propylene was invented 9 times separately in the same period of time. The scenarios of patent lawyers and court applications remained inconclusive until 1989. Finally, Paul Hogan and Robert Banks, two American chemists working at Philips Petrol in the Netherlands, were honored as the official inventors of propylene (American Chemical Society, 2023).

Propylene shows similarities with polyethylene, which we can consider its ancestor in general, and its cheapness is common to both. But propylene is a more durable material. It has a wide range of uses from plastic bottle production, carpets, plastic furniture to packaging. It is a much-needed thermoplastic in the automotive sector (Ezdeşir et al, 1999).

The following features can be listed as the main reasons why propylene is widely used in daily life. It is lightweight, it has the lowest density (0.90 to 0.92 gr/cm^3)

among the resins used in packaging, does not absorb water, it is highly resistant to compression and cracking, it is highly resistant to most bases and acids, organic solvents, and electrolytes, non-toxic, stain resistant, easy, and economical to produce (Kıralp et al., 2007).

Propylene formulations can be improved with colorants, fillers, antioxidants (antioxidants are chemicals used to prevent the material from degrading by reacting with oxygen or ozone), and UV stabilizers (UV stabilizers are chemicals used to prevent degradation by high-energy rays). Propylene powder can be obtained as plate film and fibre (Kıralp et al., 2007).

High purity production can be made for use in the semiconductor industry. Due to its resistance to bacterial growth, it is frequently used in the production of medical equipment. It is used as nonwoven yarn (nonwoven) in agriculture and fishery sectors. They are also widely used in flexible packaging (yoghurt containers, syrup bottles, etc.), construction industry (sewage pipes, pumps, etc.) and automotive industry (Kıralp et al., 2007).

2.3.1.3.Polystyrene (PS)

Polystyrene is obtained by polymerization of liquid citrene, a petroleum product. Polystyrene was first synthesized by coincidence in 1839 in Berlin, Germany by a pharmacist named Eduard Simon. Although Simon separated this material from natural resin, he did not know what he discovered. Hermann Staudinger, also a German chemist, realized that Simon's discovery was a long-chain plastic formed by the styrene molecule. Staudinger later published his theory in 1922, emphasizing that natural rubbers are long chains of small units repeating themselves and that this structure gives rubber its flexibility. He said that thermally processed Polystyrene showed similar properties to rubber. As a result of his research, Staudinger was awarded the Nobel Prize in chemistry in 1953. It was produced industrially for the first time in 1937 by Dow Chemical and introduced to the market in the USA (Staudinger, 2003).

Styrofoam© foam polystyrene, the most recognizable form of polystyrene, is a registered trademark of Dow Chemical Co. and is widely used in packaging and insulation applications (https://en.wikipedia.org/wiki/Styrofoam).

Ray Mac Intire synthesized Styrofoam© by chance while trying to find a flexible insulating material during World War II. This foam polystyrene produced by Dow Chemical Co. was 30 times lighter than normal polystyrene.

Polystyrene ranks 4th among thermoplastics in terms of production volume. It is mainly used in applications in packaging personal-corporate products, electrical-electronic products, construction, building materials, furniture, industrial and mechanical products and transport sectors (Ezdeşir et al., 1999).

Polystyrene film is used in meat and vegetable counters and packaging applications requiring transparency, polystyrene foam is used in cardboard egg cartons, household and poultry counters, food packages requiring hot or cold insulation. Solid polystyrene is used in cups, lids and disposable food packages; injection moulded polystyrene is used in cosmetics and personal care products, jewelry and photographic film containers; other polystyrene applications include audio and video cassettes, toys, flowerpots, photo frames, kitchen utensils, television and radio cabinets, smoke detectors, computer parts and building profiles (Kıralp et al., 2007)

2.3.1.4.Polyvinyl chloride (PVC)

Polyvinyl chloride is the second most produced thermoplastic polymer. It can be obtained in two main forms, rigid and flexible. It can be considered as one of the most valuable products in the chemical industry. Approximately half of the PVC produced is used as construction and building materials. In recent years, it has replaced wood, concrete, and clay as building material (Kıralp et al., 2007).

PVC was accidentally obtained by Henry Victor Renault in 1835 and Eugen Baumann in 1872 as a white solid by exposing vinyl chloride to sunlight (Ezdeşir et al., 1999).

The fact that the invention of PVC had to be made twice makes it one of the most interesting inventions. A few German entrepreneurs invested heavily in making lamps that run on acetylene gas to illuminate people’s homes and produced tons of acetylene to sell to people who bought their lamps. These events coincided almost simultaneously with the production of efficient electric generators, and the acetylene lamp business was over before it even started, leaving the entrepreneurs with tons of acetylene in their hands. In 1912, the German chemist Frizt Klatte decided to experiment with acetylene. Reactions were carried out with hydrochloric acid and vinyl chloride is obtained. But no one knew what to do with this material. The material polymerized on its own over time. Not knowing what to do with PVC, he reported his invention to the boss of Griesheim Elektron, the company he works for. The company patented this product in Germany, but they could not find a way to use PVC. In 1925, their patent expires. Independently of this, one year later in 1926, Valdo Semon, an American chemist working at B.F. Goodrich, made an excellent shower curtain from PVC, unlike the previous chemists. Mr Semon and his bosses patent this invention in the USA (Ezdeşir et al., 1999).

The most important advantage of PVC is its compatibility with a wide range of additives and this property has led to its widespread use. Thanks to the chlorine atoms in it, flammability is automatically prevented. It provides excellent electrical insulation and is used for insulation in cables. It is an ideal building material due to its strength and resistance to weather conditions. Transparent and colored, the easy transition between rigid and flexible formulations has made PVC one of the most widely used thermoplastics. Hundreds of kinds of medical, care and surgical products and their packages are made of PVC. It is also frequently used in the automobile industry due to its high performance and low cost. PVC is frequently used in window profiles, sewerage and water pipes, medical products, blood bags, cable and wire insulation coatings, floor coverings, car interior and seat coverings, packaging, credit cards, artificial leather, other coating fabrics and adhesive films (Kıralp et al., 2007).

2.3.1.5.Acrylate based plastics

The most important of this class of plastics is the material known as polymethyl methacrylate (PMMA). PMMA is a synthetic polymer of methyl methacrylate. Developed in 1928 in various laboratories, PMMA was introduced to the market in 1933 by the German company Rohm & Haas (gmbh & Co.KG).

PMMA is often used as an alternative to glass. It has half the weight of glass. It is unbreakable, more easily scratched but can be prevented by anti-scratch coatings. It transmits light more and is produced at low temperatures. It cannot block UV light, but this feature can be achieved by coating with UV blocking films (Kıralp et al., 2007).

Car headlights, ice hockey rink edges, very large windows and aquariums are made using PMMA. It can be used for laser discs and DVDs, but polycarbonates, which are more resistant to moisture, are more preferred in this field. Acrylic is used in paint production. Due to its compatibility with human tissue, it is used in the production of eye lenses and contact lenses. It is common in bone cement and denture applications (Ezdeşir et al., 1999).

Plexiglas©, made using PMMA, is produced as acrylic glass and has added many conveniences to our lives. Although it is a hard material, it softens easily in a short time at 100°C and becomes a shape that can be inserted into the desired shape. When it is cooled again, it immediately returns to its old hard state. For this reason, they are frequently used by artists and designers. Properties such as airtight, unbreakable, lightweight, burning without leaving residue make it suitable for many uses (Kıralp et al., 2007).

2.3.1.6.Polyethylene tetraphthalate (PET)

PET is a thermoplastic member of the polyester family and is generally used in the production of food, beverage, and various liquid containers and in the production of synthetic fibers (Kıralp et al., 2007).

Depending on the thickness, it can be found in the semi-rigid and rigid range. It is light, gas and moisture proof and resistant to solvents. Strong and impact resistance is high. Colorless and transparent. Light transmittance can be prevented by coating with aluminum after it is turned into a thin film. It can be reinforced with glass fragments and fibers to obtain a harder and long-lasting product.

Patented in 1941 by British chemists John Rex Whinfield and James Tennant Dickson working at the Calico Printer's Association in Manchester. The PET bottle was patented in 1973 (Ezdeşir et al., 1999).

2.3.1.7.Polycarbonate (PC)

Polycarbonate is used in unbreakable lenses for extremely lightweight spectacle lenses. It is produced by General Electric under the name Lexan©. Bayer produces polycarbonate under the trade name Makrolon© (Ezdeşir et al., 1999).

In 1953, linear thermoplastic polycarbonate was produced in Bayer laboratories. In 1957, Bayer and General Electric announced that they had independently developed a method to produce polycarbonate, and in 1960 they both started commercial production (Kıralp et al., 2007).

As unbreakable and indestructible glasses, they are used in the production of items such as food containers and baby bottles, thus contributing to the safety of ourselves and our children in our homes. Polycarbonate plastics and derivatives are frequently used in the production of carboys, water heaters, shavers, hair dryers and many similar tools we use in our homes and are preferred for their heat resistance and electrical insulation properties. In addition, the ease of coloring and shaping of polycarbonate and its derivatives makes it possible for these tools to have a more stylish and modern appearance. As it is light and durable, it is widely used in the production of mobile phones, computers, and CDs.

The common point of greenhouses and the dome of the Sydney Olympic stadium is that they are made of polycarbonate plates (Irklı Eryıldız and Aydın, 2013).

These plates are very light, almost unbreakable and provide thermal insulation and thus play an important role in energy saving. They are widely used in protective headgear, the lenses of sports and protective glasses, incubators for newborn babies, dialysis machines and health units and bring many advantages. Polycarbonate is also used in automobile parts (signals, front and rear lights, fog lights) and most of the interior design parts (Ezdeşir et al., 1999).

2.3.1.8.Nylon plastics - polyamides

Nylons are one of the most widely used polymers as fiber. In addition to its wide use in textile products, it is also possible to use it in other areas. Polyamides are naturally found in protein, wool, and silk forms. They can be artificially produced under various trade names such as nylon, Kevlar.

Found in 1935 by Wallace Carothers at Dupont, it was first used in 1938 to make toothbrush bristles. Its first real success was realized in 1940 with the production of ladies' stockings. The reason why nylon stockings were difficult to find in the following years was that America entered the Second World War a year later. Because the nylon produced was used in the production of wheels, tents, ropes, and various military materials, especially in the production of parachutes and yarn in the war. In the same period, America used nylon in the production of money with high quality paper. At the beginning of the war, 80% of the fiber use was cotton fibers and 20% was wool fibers, but by August 1945, 25% of the market was made up of nylon fibers (Kıralp et al., 2007).

Common areas of use include cord fabric in tires, textiles, toothbrush hair, fishing ropes, nets and nets, rugs and airbags, auto glass (manifolds and petrol tanks), climbing rope, machine parts, parachutes, guitar strings, tennis, and squash racket strings.

2.3.1.9.Polytetrafluoroethylene (PTFE)

The molecular structure of polytetrafluoroethylene is like polyethylene, except that the hydrogen atoms in polyethylene are replaced by fluorine atoms. In the classical definition of thermosets, cross-links between polymer chains were mentioned, but these bonds holding polytetrafluoroethylene chains do not exist. Instead, the forces of attraction and repulsion from its special nature take on the same task.

In 1969, the first polytetrafluoroethylene fibers were produced. The product obtained is a weaving known as gorateks©, which can withstand all kinds of harsh conditions, which does not pass wind and mud through the fibers, but passes air and sweat (Ezdeşir et al., 1999).

PTFE, known by the trade name Teflon©, has many application areas due to its many superior properties. PTFE is unique in chemical resistance. It is resistant to all chemical substances used in industry. No substance that can dissolve polytetrafluoroethylene below 300^{o}C has been found. The temperature of use can vary between -260^{o}C and 270^{o}C degrees. It has the lowest coefficient of friction among all known plastic materials. It is a very effective insulation material in electrical insulation. Since the plastic obtained in the production of polytetrafluoroethylene is not sticky and resistant to heat and mechanical stresses, it is formed into billets under 300-400°C temperature under high pressure in special moulds. Metals such as sodium, potassium, and fluorine gas in molten or dissolved state affect Teflon under high temperature and pressure. It is suitable for coating materials such as metal, plastic, wood, ceramic with its resistance to ultraviolet rays, ozone, humidity, temperature, salt, and similar substances (Kıralp et al., 2007).

The most used places are high temperature resistant gasket, felt, tape, valve set, sealing elements, conveyor belts and rollers, chemical resistant pipe, mixer, laboratory devices, filter, diaphragm, cable insulator resistant to electrical voltages, insulator, various insulating parts required for electrical appliances and high friction bearing parts of machine parts. Polytetrafluoroethylene alloys with glass fiber, carbon, graphite, molybdenum sulphide and bronze are produced to increase wear resistance and improve other mechanical properties. Polytetrafluoroethylene gaskets in various sizes are frequently used in industry and industrial areas (Ezdeşir et al., 1999).

GoreTex© fabric, which was used in tent manufacturing and water-resistant shoe making, was found to be bio-compatible in the following years, it was shaped as a hose and started to be used as artificial veins in the human body. Today, hundreds of thousands of people in the world continue their lives with goretex vein attachments (Kıralp et al., 2007).

Teflon is coated on the inner surfaces of kitchen equipment to give them non-stick properties. Although the chemical structure of Teflon requires it to be explained under the heading of thermoplastics, it is associated with thermoset processing methods due to its properties (Ezdeşir et al., 1999).

2.3.2.Thermosets and some thermoset types

Thermosets can transform into a cross-linked structure both at hot and room temperature. Thermoset plastics are solid at any temperature due to their cross-linked structure. The examples of thermosets are epoxy resins, polytetrafluoroethylene, polyurethane, phenol formaldehyde resins, unsaturated polyester resins. They can even be included in the group of thermosetting plastics in rubbers. Because they contain low density cross-links. The number of these intermediate bonds is adjusted according to the intended use of thermosets (Ezdeşir et al., 1999).

2.3.2.1.Epoxy resins

We use epoxy resins as coatings, paints, glues and building elements in marine, automotive, electrical, and electronic systems, and many industrial applications. The name of epoxy resins is derived from two Latin prefixes: “epi” meaning “on” and “oxy” meaning “sharp, acidic”. The history of epoxy chemistry began in the early 1900s with the discovery of epoxy monomers by the Russian chemist Prileschajev. Ciba (Switzerland), which patented the polymerization of epoxy resins in 1946, which was the work of Dr. P. Castan from Switzerland and Dr. S.O. Greenlee from the USA in 1936, produced until the end of the 1990s and then merged with the Huntsman plant in the USA (Kıralp et al., 2007).

Epoxy resins consist of two components, the main element, and the hardener. When these components are mixed in certain proportions, a hard product is obtained with high heat. There are types that can harden in a few minutes to a few hours, selected according to the application area. However, the time it takes to fully polymerize is up to one day in most of them. Due to their high chemical resistance, low permeability, and tight bond structure, they are frequently preferred in the coating area and can be applied to the surface in various ways. Brush, roller, and troweled coatings are the most common forms of these. To prevent epoxy resins from deteriorating over time by exposure to sunlight, color additives are added to them, or they are covered with a second coating such as polyurethane and latex (Kıralp et al., 2007).

Although glass fiber reinforced conventional polyester resins are cheaper than epoxy resins, epoxy resins are recommended due to some disadvantages. For example, while epoxy resin adheres well to marine elements such as wood and steel, polyester resin leaves bubbles on the surface and adheres poorly to the elements because it is more self-adhesive. During application, polyester resins emit a strong odor compared to epoxy resins. On the other hand, since most of the epoxy resins do not contain solvents, it is an important advantage to apply them together without damaging the foam surfaces.

Epoxy resins are used as “matrix” in composites and carbon fiber is used as “reinforcement” in composites. Formula 1 car bodyworks are high-tech products, shock absorbing and highly resistant to impacts. Similarly, aerospace technology, which requires high performance and low weight products, also utilizes epoxy resins (Ezdeşir et al., 1999).

Users can increase the strength of epoxy resins by using fillers suitable for their purpose. Powdered colored glass powders, silica, sand, aluminum oxide are examples of these fillers. The abrasion resistance of epoxy resins used together with sand in floor coatings increases several times compared to their use alone (Kıralp et al., 2007).

Since some types of epoxy resins do not lose their adhesion and coating properties even in sea water, they are used to close the cracks caused by accidents in marine vehicles in a short time and are known as one of the most important parts of emergency equipment in maritime. The strong bond of epoxy resins with wood and steel surfaces has enabled this thermoset to be used not only in repair but also in boat manufacturing.

Epoxy resins are insulators under normal conditions; when applied together with conductive polymers, semiconductor materials are obtained, and when applied with metals such as tin, conductive materials are obtained (Ezdeşir et al., 1999).

2.3.2.2.Phenol-formaldehyde resins

Bakelite, the best-known type of phenol-formaldehyde resins, is a thermoset plastic formed by phenol and formaldehyde chemicals in acidic environment. Bakelite is the US industrialist chemist Leo Hendrick Baekeland, who found it in 1909 and named it and pioneered the establishment of the modern plastics industry. The reason why he is considered as the father of plastic is that the Bakelite he discovered is the first synthetic plastic.

Bakelite is a glossy, heat resistant, insulating, and hard material. Thanks to these properties, it has remained a strong alternative for a long time against the materials that will replace it in the past years. For example, during World War II (1942), there was a shortage of raw materials due to the use of metals as war materials in America. As a result, the small denominations of coins (cents) were made of bakelite instead of metal for one year. Today, although it has been replaced by modern materials in many areas, its use in the handles of kitchen utensils is still indispensable. Bakelite was frequently used in heat-resistant furniture, hair dryers, toys, table and wall clocks and many other areas until the middle of the second half of the 19th century (Kıralp et al., 2007). The calculator, desk clock, camera, and radio from the 1930s-1940s shown here are made of bakelite. Bakelite continued to be used in the windings inside radios and electronic devices in later years.

Today, bakelite has found a modern use (Figure 2.5); it is frequently used in ornaments and jewellery such as necklaces, brooches, earrings, and bracelets (Ezdeşir et al., 1999).

Figure 2.5. Some bakelite products

2.3.2.3.Polyurethane (PU)

The polyurethane is obtained by mixing two or more chemical liquids containing cyanate and alcohol groups in certain proportions and then cross-linking them. Polyurethanes offer a wide range of products from hard to soft. The most common use of polyurethane is foam form. In applications with direct spraying on the surface, the air entering the spray gun mixes with the polyurethane particles coming from the feed unit, forms foam and covers the surface.

Polyurethane foam is an assembly material that provides filling and sealing for many building materials and expands with moisture in the air. Due to its rapid hardening, it provides effective insulation against moisture and dryness. It is completely resistant to water. It is used in the insulation of door, window frames and pipe systems that are required to be fixed by compression, sealing roof gaps, filling cracks and gaps in concrete floor surfaces (Ezdeşir et al., 1999).

Polyurethane plates are produced as plates in sandwich panel machine. These polyurethane plates are also sandwiched between wood or metal plates and used in exterior cladding or portable house construction.

The fiber form of polyurethane is Spandex© elastic and was first made by Josef Shivers (Dupont laboratories) in 1959. Lryca©, used in underwear and socks, is one of the commercial names of Spandex©. Spandex can be stretched up to 5 times its own length without breaking. Although it has weaker strength than rubber, it is longer lasting. It is both resistant to body lotions, water, sweat and is frequently used in the clothes of athletes due to its flexible, soft, smoothness (Kıralp et al., 2007).

Polyurethane may cause undesirable results when exposed to high temperatures. The main cause of the odour rising with the temperature in the interior of the cars in the summer months is the small molecules coming out of polyurethane and it is important to ventilate the environment immediately in terms of health. It is thought that the accident with the explosion of the Challenger spacecraft shortly after its launch on 28 February 1986 was caused by the ignition of the particles emitted by the polyurethane used in the insulation of hydrogen fuel tanks after exposure to high temperature (Ezdeşir et al., 1999).

2.3.2.4.Unsaturated polyester resins

Polyester plastics are condensation polymers containing ester (esters are organic compounds containing C-O-O-C groups) functional groups in their main bonds and are divided into two as saturated and unsaturated. Unsaturated polyesters tend to form cross-links because they contain double bonds with ester groups and the resulting product is thermoset. Although they contain ester groups, polyesters that do not contain double bonds do not form cross-links due to their saturated structure. These can be exemplified by polyethylene tetraphthalate and polycarbonate plastics in the thermoplastic section (Kıralp et al., 2007).

The first synthetic polyester, glycerine phthalate, was used in the First World War to obtain waterproofing properties. Natural polyesters have been known since the 1830s. The common use of the word polyester refers to fabric made from polyester fiber. Polyester fibers are often used in combination with cotton fibers to produce garments with better properties.

Since unsaturated polyesters do not have strong cross-links compared to other thermosets, they are not used alone due to their high fluidity and weak strength. Additives increase the strength by forming a reticulated structure in the plastic. One of the most known additives is glass wool. Thanks to its good resistance to environmental conditions and easy processability, unsaturated polyester resins have found application in a wide variety of fields. They are mostly reinforced with glass fiber and used in the production of marine boats, car bodies, discharge pipes and water tanks. One of the most common areas of use is chemical tanks and pipes that require chemical and heat resistance, electrolysis containers, coating surfaces against corrosion. The point to be considered is that they are used together with phenolic additives to prevent the glass fiber or filler with which they are used from being affected by the corrosion environment (Kıralp et al., 2007).

The bridge in Kolding, Denmark is made of unsaturated polyester backed by glass fiber. It was erected in a short time like 18 hours and although it is 40 meters long, it weighs only 13 tons. It is planned to serve for a hundred years without being affected by rain, salt, and ice. Its carrying capacity is around 500 kg/m^2 and it can allow vehicles weighing snow machines to pass.

https://commons.wikimedia.org/wiki/File:Fiberline_Bridge_Kolding_Denmark_2013c.JPG

2.4.Production Methods of Plastics

Evren Çağlarer

Plastic processing methods basically exhibit differences according to the structure of the polymer to be used. In this subchapter, plastic processing methods are analyzed under two main categories as thermosets and thermoplastics.

2.4.1. Thermoplastic processing methods

2.4.1.1. Extrusion

Extrusion means forcing the molten material to flow through a continuously shaping device. In the plastics industry, extrusion is the method applied for the continuous production of films, sheets, rods, pipes, and various profiles at high capacities using devices called extruders.

Extrusion involves mixing the plastic raw material, which is made fluid by heat and pressure, after adding additives (colorants, reinforcements, preservatives, etc.).

As a principle, extrusion works with a mechanism like meat grinders. The raw material is continuously fed into the extruder at a certain speed through a part called the feed hopper. The fluidizing process occurs by rubbing the plastic raw material against hot surfaces by means of an auger rotating continuously and at high speed in a heated barrel. The screw transfers the molten plastic through the barrel while mixing and compressing it (Figure 2.6).

The forming process takes place in the part called the head, which forms the last point of the extruder. The molten plastic takes shape by passing through here with the help of the driving force created by the compression effect. The plastic leaving the extruder at this point can be produced as pipe, rod, film according to the shape of the mould placed at the end of the nozzle (Akyüz, 2001).

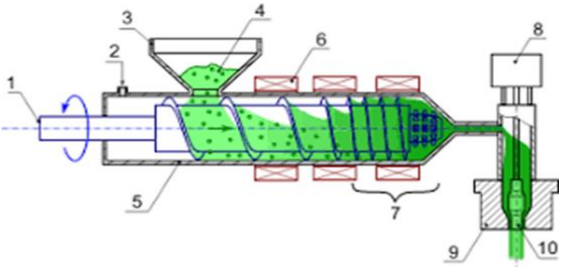


Figure 2.6. Extrusion-blow moulding of polymers: 1. Reciprocating screw; 2. Compressed air; 3. Hopper; 4. Granules; 5. Barrel; 6. Heaters; 7. Grinding, mixing; 8. Actuator's hydraulic generator; 9. Draw plate; 10. Core/punch. (https://commons.wikimedia.org/wiki/File:Principe_extrusion_soufflage_polymere.svg)

The extruder barrels are made of high hardness special steels. Heating is done with hot oil or electric heaters. The temperature can be controlled separately in various parts of the barrel throughout the extruder. Thus, the manufacturer is given the opportunity to control the fluidity of the plastic. In general, the section where the plastic raw material is fed into the extruder is relatively cold, while the other parts are warmer and the head area is set to be the hottest (Ezdeşir et al., 1999).

The screw is the most important part of an extruder. It is connected to a powerful motor at the end and the speed of the motor can be controlled. There is usually a small opening between the emphasis and the barrel, which can be expressed in millimeters. As the plastic is forced through this opening by the screw, melting and mixing occurs at the same time (Akyüz, 2001).

The extrusion process is the first step in many other plastic processing methods. For example, the "film inflation" method, in which the polythene bags we use in daily life are produced, is one of them. In this processing method, the polyethylene melted by the extruder mixes with hot air as soon as it leaves the head area and becomes thinner at the same time as it swells upwards like a balloon. When the desired thinning is achieved, it is cooled and solidified and then wound on a reel.

https://upload.wikimedia.org/wikipedia/commons/thumb/7/7b/Film_extrusion.jpg/449px-Film_extrusion.jpg?20090305170709

Many products we use in current life are produced by using extrusion method. The main ones are PVC profiles used in windows, films made of chocolate and confectionery packaging, plastic sheaths of electrical cables. Additionally, various extrusion systems are also used for purposes such as coloring plastics, adding additives, mixing two plastics (Ezdeşir et al., 1999).

2.4.1.2.Injection moulding

Injection moulding is a plastics processing method based on the principle that thermoplastic materials are melted and fluidized, then shaped under pressure in a cold or relatively hot mould, followed by cooling and solidification. They can be used in the production of very detailed and small parts such as mobile phone covers as well as rough and large parts such as picnic chairs. It is a widely used processing method in the plastics industry, especially due to its features such as the possibility of producing many parts in a short time and fully automatic operation (Akyüz, 2001).

The devices used in injection moulding technique mainly consist of feed hopper, barrel, auger, ejector piston and mould. The Figure 2.7. below shows schematically the parts of an injection moulding machine and how they are processed.

In the first stage, the screw takes enough raw material from the feed hopper to fill the mould by rotating and just like in extrusion, it rubs against the hot barrel surfaces, melts and fluidizes it and transfers it towards the cavity at the end. In the second stage, the molten plastic accumulated in the cavity at the end of the nozzle is pushed towards the mould by the auger with the forward movement of the piston. The screw remains in this position until the plastic in the mould solidifies. In the last stage, new raw material is taken from the feed hopper with the reverse movement of the piston. At the same time, the mould is opened, and the product is ejected through a special device. The second injection period starts with the closing of the mould (Akyüz, 2001).

Practically every thermoplastic can be processed by injection moulding method. Many products such as disposable cups, combs, electrical switches, sockets, toys, television etc. that we use in daily life, outer cases of goods, plastic garden tables and chairs are processed by this method (Ezdeşir et al., 1999).

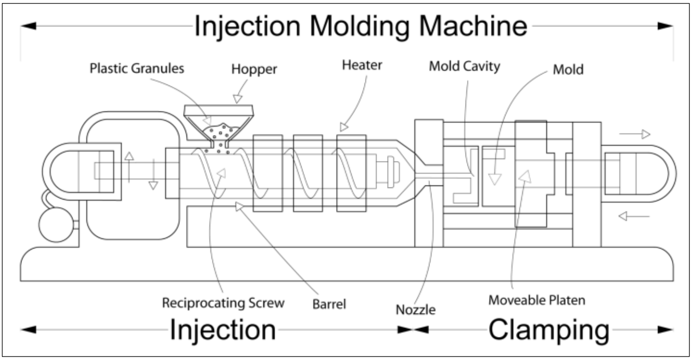


Figure 2.7. Injection moulding machine (https://commons.wikimedia.org/wiki/File:Injection_moulding.png#/media/File:Injection_moulding.png)

2.4.1.3.Blow moulding

Blow moulding is a widely used processing method for the manufacture of hollow parts. Especially pet bottles and jerry cans are produced by this method (Figure 2.8).

Figure 2.8. Production of a plastic bottle from raw dummy to blown up PET bottle (https://commons.wikimedia.org/wiki/File:Plastic_bottle.jpg#/media/File:Plastic_bottle.jpg; By Nicole Gordine - Own work, CC BY 3.0; https://commons.wikimedia.org/w/index.php?curid=16844093; https://commons.wikimedia.org/wiki/File:PETling.jpg#metadata)

In this method, injection moulding is used to inflate the tubular plastic parts called parison (preform) in the mould with hot air. The hollow product, which takes the shape of the mould, cools and solidifies with the opening of the mould. The stages of this process can be seen in the Figure 2.9.

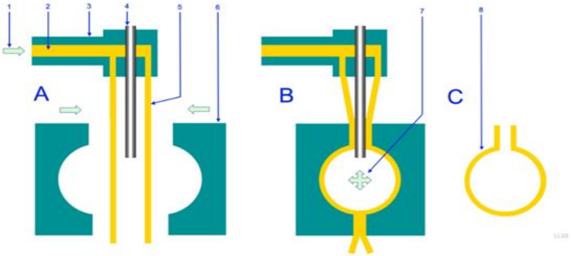


Figure 2.9. Principle drawing of the blow moulding process. 1. Feed from extruder; 2. Molten plastic; 3. Extruder head; 4. Air pipe; 5. Preform (parison)/tubular from hot plastic; 6. Mould; 7. Air pressure; 8. (Final) product (https://commons.wikimedia.org/wiki/File:Blow_molding.png)

The parison is poured into the mould, the parison softens under the influence of the hot air blown into the mould and starts to inflate. The inflated parison takes the shape of the mould. The mould is opened, and the bottle is taken out (Ezdeşir et al., 1999).

2.4.1.4.Rotary moulding

This processing method is also used to produce solid and hollow objects, as in blow moulding. However, the products obtained in this method are generally large parts. Garbage containers, storage tanks, fuel tanks in automobiles, playgrounds in parks, golf cart bodies, etc. are made by rotational moulding (Akyüz, 2001).

In this method, the raw material in powder form is poured into the mould. The mould is then rotated in a hot oven at high speed in all directions. Meanwhile, the plastic, which becomes fluid under the influence of temperature, flows all over the mould and covers the inside of the mould.

After this process continues for a certain period, the mould is removed from the oven and allowed to cool. The solidified product is removed by opening the mould (Ezdeşir et al., 1999).

https://en.wikipedia.org/wiki/Rotational_molding#/media/File:Rotational_Molding_Process.svg

2.4.1.5.Fibre pulling

It is the method of producing synthetic fibers such as polyester and polyamide (nylon), which are frequently used in daily life, especially in the textile weaving sector. In this method, the plastic melted by the extruder is passed through a head with many fine holes on it. The resulting fibers are drawn at high speed and thinned and then cooled and mixed. These fibers are then wound on bobbins to make yarn (Ezdeşir et al., 1999).

The diameter of the holes in the head and the drawing speed determine the thickness of the yarn to be produced. The thickness of the fibers is expressed in a measure called “denier”. Denier is equal to the weight of 9000 meters of yarn. In other words, high denier textile products are woven from thicker fibers (Akyüz, 2001).

2.4.2. Thermoset processing methods

2.4.2.1.Hand laying method

This is a method for making rough parts from thermoset plastics. As the name suggests, everything is done by the hands of the worker. In this method, unsaturated polyesters are usually used together with glass fiber woven. Unsaturated polyester is poured onto the glass fiber woven by hand into the mould and then the air is removed with a brush. It then solidifies over time due to the hardener inside. The solidification process is accelerated by applying heat in some applications. Heat application process is called cooking in the industry. With this method, parts such as bathtubs, yachts, sports car bodies can be manufactured (Ezdeşir et al., 1999).

2.4.2.2.Mould press

In this processing technique, the thermoset plastic placed in the moulds in the hot press is hardened by cooking with temperature under the pressure applied by the press. With this technique, which is generally used in the manufacture of medium-sized parts, larger objects such as melamine dinner plates, vases used in our homes, as well as larger objects such as aircraft parts can be made.

2.4.2.3.Fibre winding method

In this process (Figure 2.10), glass fibers are passed through a thermosetting resin bath and then wound on a rotating drum in all directions. After the winding process, the thermoset plastic is cooked and hardened by applying heat. The mandrel on which the fibres are wound is then pulled out from the center and a hollow product is obtained (Çağlarer, 2023).

Using this method, silo tanks, pressure-resistant pipes, sports equipment, aircraft parts and some military equipment can be produced.

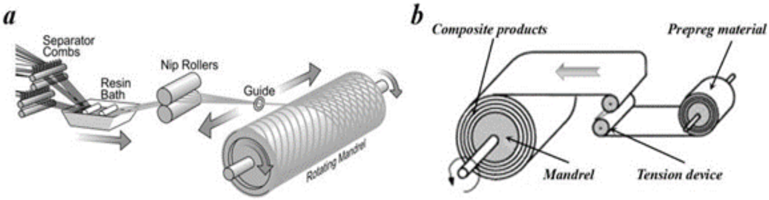


Figure 2.10. Basic winding arrangement diagram; (a) wet winding method; (b) prepreg winding method (Ma et al., 2018)

2.5.Usage Areas of Plastics

Evren Çağlarer

Plastics, thanks to their physical and chemical properties, can respond better than other materials to many features that both users and manufacturers want and need. Therefore, plastic materials have found a wide range of uses in many areas such as construction, textile, food, automotive, agricultural sector.

The packaging industry is a very large industry branch, and the plastic packaging industry has an important place in the economies of countries. Plastic packaging is used in the packaging of pesticides, electronic devices, foodstuffs, mineral oils, detergents, medical drugs, chemicals, cologne, and cosmetic products. Plastic packaging has many benefits such as sterile storage of medical products and medicines, extending the shelf life of foodstuffs such as meat and vegetables, and protecting sensitive technical products from damage. Consumers demand packaging materials that are more convenient, in different sizes, easy to open, but at the same time contain child-safe devices, are environmentally friendly and provide minimal cost increase in the price of the packaged product.

The main polymers used in the packaging industry are polyethylene, polystyrene, polypropylene, PVC, and polyester. Low density polyethylene is the most used plastic type in our homes. It has many uses such as bleach, detergent and shampoo bottles, motor oil bottles, garbage bags. High density polyethylene is used in milk, yoghurt, ice cream, margarine storage containers and packaging of cleaning products. PET is used in the packaging of carbonated drinks, water, soft drinks, and oil bottles. Since it has good heat resistance, it can be used as containers for foods to be heated in microwave ovens, and it is also used in the packaging of hot filled foods (such as jam) during production. Since polypropylene has a high melting point, injection moulded polypropylene is preferred for making plastic cups, large basins, and buckets. Polystyrene is used in hot beverage containers, plates, egg viols, medicine bottles. PVC is used in transparent food containers, soda bottles, packaging of oils, shampoos, some chemicals, health, and cosmetic products. Polystyrene foam is widely used in the packaging of devices that may be damaged during transport (Plastipedia, 2023).

The construction sector is the second sector that uses the most plastic after packaging. They combine excellent strength-to-weight ratio, durability, cost effectiveness, low maintenance and corrosion resistance, making plastics an economically attractive choice in the construction industry.

Plastics used in construction are mainly used for gaskets, profiles (windows and doors), pipes, cables, floor coverings and insulation. Potentially plastics have more uses as they do not rot, rust, or need regular repainting, are lightweight, robust, easily shaped, enabling them to be easily transported and moved around the site.

Pipe is the largest user of polymers in construction, consuming 35 per cent of production. Large diameter pipes for cabling, rainwater goods, sewerage, drainage and drinking water are produced from PVC and polyethylene (Plastipedia, 2023).

Cladding and Profiles made from PVC-U for windows, doors, mouldings and skirting boards, exterior cladding using phenolic are replacing wood with traditional resins with minimal fire risk.

Insulation is produced from Polystyrene rigid foam, which is usually incorporated into panels or compressed into the construction of walls and roofs. Insulation combines light weight and strength and is easy to install, enabling contractors to meet energy saving regulations.

Seals, main construction uses insulation strips, span seals, gaskets and expansion joints are made from elastomers. The polymers used are chloroprene and EPDM, which are weather resistant, resistant to deformation and retain elasticity. PVC is used as a membrane for windows and doors, as well as for roofing and cladding. In addition, 250,000 tons of polymers are used as a base for adhesive systems and sealants (Ezdeşir et al., 1999).

The cost-effective and safe transport of people and goods is vital to our economy. As modern modes of transport have evolved to meet increasing demands for safety, environmental protection and speed, the use of plastics in transport manufacturing has increased significantly.

All modes of transport require energy to operate and fuel accounts for a significant proportion of operating costs. Reducing the weight of cars, aero planes, boats, and trains can significantly reduce fuel consumption. The light weight of plastic therefore makes them invaluable to the transport industry. Using 105 kg of plastic instead of metal in a 1,000 kg car can save up to 7.5 per cent of fuel (Plastipedia, 2023).

The automotive industry uses plastics in a wide range of areas. Since the beginning, the use of plastic components in cars has increased from a few kilos per car to an average of 105 kilos. Initially, plastics were used because they offered good mechanical properties, including self-coloring, combined with an excellent appearance. Increasing costs have led to plastics being used for their ability to be moulded into components with complex geometries, to replace several parts made from other materials and to offer equipment that allows easier assembly, helping to reduce costs on the assembly line. The replacement of many parts used in the past by plastic has caused vehicles to become lighter. This has led to fuel savings in vehicles (Plastipedia, 2023).

In automobiles, plastic parts are used in the front console, control panels, floor coverings, fuel tanks, bumpers, fenders and in recent years as engine parts. The use of carbon and glass fiber reinforced plastic materials in the exterior of cars is also increasing. Polyamide and polyethylene are preferred in the production of gas and clutch pedals, and polypropylene is preferred as a battery box. Monolithic fuel tanks are made of high-density polyethylene by blow moulding method. Polyetherketone has started to replace metal parts exposed to abrasion and heating in the automobile industry due to its resistance to high temperature and abrasion. The production of car tires is an area where polymer technology is used at the highest level and polyisoprene is used as rubber and polyamide is used in cord fabric production. Polychloropyrene is widely used in the production of hoses in the engine part of the car. Glass fiber reinforced polyamide is preferred for making oil filters of automobiles. Polyamide is also used in the production of gear lever. Fibres made of polyamide are also preferred in the production of seat belts. Distributor cover, gears in gearbox can be made of phenol and formaldehyde resins (Plastipedia, 2023).

In railway locomotives, wagons and other carriages, the materials used must be resistant to wear and tear caused by intensive use. The durability of plastic is one of the factors that make it the first choice for engine and carriage panels, flooring, luggage racks, seating, and doors.

In the marine industry, the ability of plastics to withstand the harsh marine environment makes them indispensable in all types of marine vessels, from ocean liners to sailing boats. Plastics do not wear or warp and require less maintenance than other traditional materials to remain attractive and in good working order.

Aviation products' aerodynamic requirements demand maximum design flexibility and minimum weight. Plastics can be formulated to meet a wide range of specifications and are ideal for components with smooth curves. Composites are widely used in wing skins, nacelles (a type of skin that is separate from the airframe and carries equipment such as engines, fuel, or equipment), fairings, ailerons and helicopter rotor blades in commercial applications as well as panels for military jets and helicopters. Plastics are also found in aircraft interiors, for example in bulkheads, stoves, stair units, seating, and upholstery.

Perspex aircraft canopies to the new A380 Airbus plastics in the 1940s made major contributions to aircraft technology. The increased use of plastics in aircraft enables less fuel to be burned by saving weight, resulting in a reduction in emissions, which in turn reduces operating costs. Strong and lightweight plastics made it possible to launch the world's largest commercial aircraft in early 2005. About 22% of the Airbus 380 fleet is built from plastics reinforced with carbon fiber. The aircraft has a composite center wing box, a crucial structure that connects the wings to the fuselage. Carbon fiber reinforced plastics are also used for horizontal stabilizers, ailerons, aft fuselage section and roof beams. Impact-resistant thermoplastics are used on the wing leading edges. Thanks largely to the use of plastics, the A380 burns fuel per passenger at a rate comparable to an economical family car.

Jets made of plastic composites require far fewer parts. Since plastic weighs less than aluminum, aircraft burn less fuel. It reduces fuel consumption by approximately 20%. The Boeing787's three plastic composite fuselage sections provide superior strength and allow the passenger cabin to withstand higher pressure. Maintenance costs are 30% lower than aluminum aircraft. Plastic composites make up 100% of the 787's exterior and 50% of all materials in the aircraft (Plastipedia, 2023).

Spaceship One, the first private spaceship to fly into terrestrial orbit, made extensive use of carbon fiber reinforced plastics to escape gravity while keeping weight low.

In the textile sector, plastics are mostly used in fiber form. Synthetic fibres are made from polymers, and these are made ready for use by weaving, knitting and nonwoven surface forming techniques. The most used polymers as fibres are PET, polyamide, polypropylene and polyacrylonitrile. Lycra (polyurethane) and kevlar (aramid) have specific uses in polymers integrated with their trade names. Lycra is used in flexible fabrics. Bulletproof vests are made of kevlar. The carpets we use in our homes are made of PET, polypropylene, polyamide. Non-wrinkling fabrics are made by using cotton and polyester as a mixture (Ezdeşir et al, 1999).

In the electrical and electronics industry, plastics are used in many areas from main switches to cables and substations. Moulded housings made of plastic are used in televisions, radios, computers, mobile phones and many electronic devices. In addition, some circuit elements are coated with plastic. Polystyrene, epoxy, polycarbonate are polymers used quite frequently in the electronics industry. Polycarbonate is used in the manufacture of CDs. Polyethylene and cross-linked polyethylene are used in the coating of PVC cables, epoxy resins are the most preferred polymers to produce printed circuit boards. Phenolic resins are used in the production of electrical switches used at home (Plastipedia, 2023).

In sports, balls used in many sports played with balls such as football and basketball are made of plastic. Cellulose nitrate is used in the production of billiard balls. Very light and robust tennis rackets are made of carbon nylon composites. Carbon fiber reinforced composites are used in bicycle construction, thus very light bicycles can be produced. Elastomers are used in the construction of running tracks to increase comfort and reduce injuries. Artificial grass made of polypropylene is used in football fields. The most used polymer in the soles of sports shoes is polyurethane. Polyethylene is widely used in the construction of products such as slides and climbing modules in children's playgrounds.

In the toy and game sector, there are many polymer usage areas, especially polyethylene, polystyrene, and polypropylene. Polyethylene is mostly preferred in the production of Legos. Polyamide is preferred in the production of dolls' hair, and engineering plastics are preferred in the production of expensive toys such as model airplanes and model cars. Carbon fiber reinforced composites are preferred for the exterior of model aircraft.

In the agricultural sector, standard thermoplastics such as PVC and polyethylene are mostly preferred. We come across plastic products in many areas from greenhouse covers to the construction of flowerpots and irrigation pipes. Polypropylene and PVC are mostly used in the construction of irrigation pipes. High density polyethylene is preferred in the construction of crates used in the transport of products such as fruit and vegetables. Plastics made of PVC are preferred in the construction of fences and railings. In the agricultural sector, load-resistant bags and sacks are needed for the transport of fertilizers, seeds, and cattle feed. These bags or sacks are mostly obtained by weaving strips made of polypropylene. Extruded polyethylene nets are used to protect the crop against birds, rodents, and deer and to provide shade. Polyurethane and polystyrene foams find many applications in agriculture and horticulture due to their low density and excellent thermal insulation properties. Transparent PVC, polymethylmethacrylate, glass reinforced polyesters and polycarbonate are used in greenhouse cover construction.

In the medical sector, the percentage of plastics used is low compared to other sectors, but a life without polymers is unthinkable in terms of hygiene. Plastics are also used in the medical field due to many advantages such as hygienic, robust, light, protective, disposable, flexible application. It allows the reconstruction of human tissue (such as artificial bone and constructive cosmetic surgery), provides ease of application in treatment (such as artificial heart, serum hoses, blood bags, syringes, drug packaging, organ transplant packaging). One of the most widely used polymers in the medical field is polycarbonate. Polycarbonate is used in many medical devices thanks to its properties such as biocompatibility, high strength, good heat resistance. Polycarbonate is used in portable respiratory therapy devices, dialysis devices. PVC rods can be used in the construction of blood and urine bags, cannulas, and proper union of broken bones. Polymethylmethacrylate is used in the production of intraocular lenses. Shoe covers, catheters, band-aids, enema sets are also made of plastic (Ezdeşir et al., 1999).

2.6.End of Life of Plastics

Charlotte Thiel

“Refuse what you do not need; reduce what you do need; reuse what you consume; recycle what you cannot refuse, reduce, or reuse; and rot the rest.” Bea Johnson

With this statement, the U.S. environmental activist Bea Johnson sums up what environmentally compatible resource management adapted to human coexistence and society should look like. Literally translated, she calls for doing without what is not needed, reduce what is needed, reuse everything that is consumed and recycle everything else that can neither be avoided, reduced nor reused. Everything left over must be composted. Therefore, this subchapter covers the general end of life scenarios for plastics.

2.6.1. Why looking at the end of life?

Plastics are criticized in particular because of their high volume of waste and the generation of microplastics. The uncontrolled discharge of plastic waste into the environment is referred to as “littering”. Littering can be further differentiated in “marine littering” and “urban littering”. Marine littering describes the accumulation of plastic waste, which mainly consists of packaging material and waste from fishing and shipping, on coasts and in the sea (Dahlmann et al., 2022). Urban littering involves disposable items such as plastic and paper bags that are not properly disposed of by consumers. In addition to the negative aesthetic impact, it leads to environmental pollution (Anthony and Andredy, 2003). Microplastic pollution is related to “littering”. This refers to solid plastic objects that enter the environment indirectly or directly through humans. A distinction can be made between primary and secondary microplastics. Primary microplastics are released either during the production of the product (e.g. cosmetics) or only in the course of the use phase (e.g. through tire abrasion, the washing of synthetic fibers or the weathering of paint). Secondary microplastics are formed by the fragmentation of plastics in the environment (Bertling et al., 2018). Serious consequences for biodiversity and the health of living organisms are attributed to microplastics (Dahlmann et al., 2022). To prevent waste from being created in the first place, we need to use our resources more responsibly. An essential part of this is thinking about the end of life from the very beginning. In the sense of the circular economy, products should be kept in the technical cycle for as long as possible. Through reuse and recycling, the material is to be preserved for as long as possible in accordance with current regulations, Figure 2.11, thereby reducing waste and the consumption of resources.

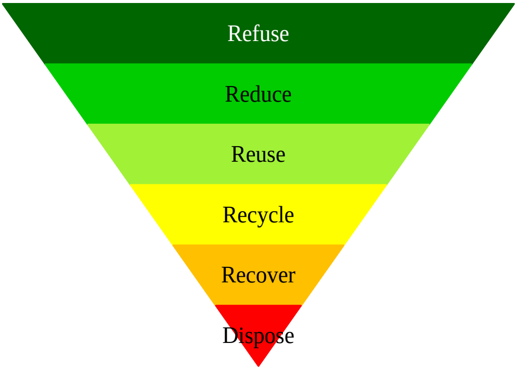


Figure 2.11. Waste hierarchy from most preferable (refuse) to least preferable (dispose waste), (adapted from (Recycling.com, 2019)

In this context, the primary goal is avoidance. If this is not possible, preparation for reuse, recycling, and other recovery (e.g., energy recovery) should follow. The use of (bio)degradable polymers can reduce environmental pollution. Biodegradable polymers can be composted or anaerobic fermented or can be used for recovery of energy. Disposal (landfilling) should be avoided (Figure 2.11), (Gesetz zur Förderung der Kreislaufwirtschaft und Sicherung der umweltverträglichen Bewirtschaftung von Abfällen – Kreislaufwirtschaftsgesetz - KrWG, 2012). The different end-of life options for plastics are shortly explained in the following. The best option is to prevent the formation of plastic waste. Therefore, single-use goods should be maintained to a minimum.

For example, (EPCM, 2023) estimated that using a reusable bottle that can be filled rather than purchasing bottled water would significantly reduce the amount of plastic waste. Note that plastics can have different names. For example, microplastics are used in cosmetics under various names like polyethylene (PE) or polyquaternium (PQ) which can hide the small particles. Therefore, it is important to have a look at the content of a product.

2.6.1.1.Refuse

The best option to avoid pollution, is not to cause it in the beginning. For example, you can seek non-packaged products and ask yourself what you really need. Repair, reuse and share whenever possible. The strategies of reducing plastics are discussed in the following subchapter.

2.6.1.2.Reduce

Plastic waste arises either during the use of products (for example car tires or outdoor paints, varnishes) and by the unnoticed detachment of plastic particles, when the product is broken or when it lost its purpose (end of use). Inputs of plastics into the environment can be reduced by replacing them with alternatives (substitution), by sharing products or by using products with longer service life or by a general reduction in consume. When substituting a product with a different material the advantage of the replacement must be proven in each individual case by a life cycle assessment and cannot be assumed.

For example, packaging should be dispensed wherever possible. If this is not ecologically sensible, because the packaging has an important function, the optimization of the packaging design and the substitution with other materials should be considered. Optimization of the packaging design can be achieved by reducing the material thickness or the use of material-efficient production or packaging techniques. Other approaches are the combination of individual products into larger packaging units or, on the packaging side, by reducing the air gap within the packaging.

2.6.1.3.Reuse

When avoiding and reducing of waste is not possible, circular products that can be reused should be preferred to recycling (including waste processing) recovering, treatment of waste and disposal. Fundamental to reuse is that not only the material but parts of the product are retained. It is estimated that since the 1950s no more than 10% of plastics have re-entered the value chain (i.e., have been recycled or reused) (Geyer, 2020).

2.6.1.4.Recycle

In recycling, a distinction is made between mechanical, chemical, and thermomechanical processes. In mechanical recycling, the collected products are sorted, crushed, washed and re-granulated. The molecular structure is retained, but the product is destroyed. Post Industrial Recyclates (PIR), which are produced during the production phase and are therefore very pure and in a clean condition, are particularly suitable for this purpose. If, on the other hand, Post Consumer Recyclates (PCR) are used, the sorting and cleaning effort is significantly higher to separate and clean the mixed materials. The possible molecular degradation and leaching of additives is a problem of mechanical recycling. This can be counteracted by adding non-recycled polymers. The aim of chemical recycling is to break down and decompose the structure of the polymer into its basic building blocks (monomers). Since it is considerably more costly in terms of energy than mechanical recycling, it only makes sense under certain conditions for individual plastics (e.g., PS, PMMA and PE) (Kirchherr et al., 2018). Thermochemical recycling renders waste plastics suitable for reuse as a raw material in the chemical industry. The result of the pyrolysis process is a new raw material that can be used in a so-called cracker (or its purification train). Another approach is “design for recycling”. Here, recycling is already considered during product development. This means that mono-material solutions are preferred, and the material selection is made under the aspects of dismantlability, separability and sort ability in the recycling process (Kirchherr et al., 2018).

2.6.1.5.Recover

Recover or Downcycling is a recycling process in which the final product has a lower quality and functionality than the original product. This loss of quality is often caused by the presence of foreign elements in the end-of-life materials. Plastics, for example, exhibit this end-of-life potential, and their recycling is associated with a loss of quality (Hillebrandt et al., 2021).

2.6.1.6.Upcycle

If the product gains in value through recycling, it undergoes upcycling. This value gain is associated with an increased energy input compared to recycling. From an ecological and economic point of view, this additional effort is only justifiable if the secondary product is superior to the primary product in terms of its properties (Müller, 2018).

2.6.1.7.Dispose - organic waste processing

(Bio)degradable materials can be used for organic waste treatment. Organic recycling can be realized as composting, i.e., biological transformation of the biowastes under aerobic conditions into CO_2, H_2O, and biomass (organic matter) or anaerobic digestion of the organic fraction of wastes in the presence of microorganisms, with the biogas production (Karan et al., 2019). The obtained compost can be utilized as the soil fertilizer (Wojnowska-Baryła, et al., 2020).

Energy recovery or **incineration** is used when neither reuse nor recycling is ecologically or economically feasible. If the plastic waste is then used as fuel for energy generation, appropriate filter technology must be used for direct incineration. These prevent toxic dioxins, which can be produced during incineration, from being released into the environment (Kaiser, 2021). On closer inspection, it becomes clear that energy recovery does provide a further use, but the waste is removed from the cycle. This means that only a reduction in waste can be achieved and not a conservation of resources, as is the case with recycling. Consequently, reusing, mechanical and chemical recycling should be increasingly promoted.

In the case of **landfilling**, as in the case of uncontrolled disposal of plastic waste, there is a possibility that additives will be dissolved out of the plastics by rainwater or seawater (leaching process). These spread through the water cycle and can enter the food chain. Important parameters for the leaching process are the temperature, the swelling capacity of the material, the pH value, and the storage density (Türk, 2014). The importance of considering plastics and their impact on the environment over the entire life cycle is illustrated here. The additives can pose a risk to the environment not only during production and use, but furthermore during landfilling.

2.6.1.8.Challenges

Incinerations causes CO_2 outflow in the environment, whereas landfilling causes different groundwater issues and should therefore be avoided in future. For this, increasing knowledge and design to reuse/remain/recycle are needed. Currently, mixing of different polymers or blending polymers with other materials like metal or glue complicate reuse and recycling. It is easier to dismantle materials when this is already considered at the design stage. This demands a specialized understanding of the subject matter and skills. Furthermore, reusing and recycling can be challenging and therefore expensive.

2.6.1.9.Outlook

Plastics production is subject to constant growth. The availability of fossil raw materials is in contrast. The point in time at which demand reaches or exceeds availability is disputed. Note, however, that fossil fuels are finite resources. Consequently, there is a need to establish and further develop alternative carbon sources. In the case of plastics, this can be achieved using bio-based feedstocks.

Highlights

- The development of plastic materials started with the use of natural materials (such as gum, shellac) with the properties of plastic, and then continued with the development of chemically modified natural materials (such as rubber, nitrocellulose, collagen, galalite.
- Plastics can be classified according to various criteria. They are generally divided into cross-linked and non-cross-linked plastics according to their chemical bond structure. Thermosets and elastomers are crosslinked. Thermoplastics are not cross-linked.
- Jets made of plastic composites require far fewer parts. Since plastic weighs less than aluminium, aircraft burn less fuel. It reduces fuel consumption by approximately 20%.
- The common point of greenhouses and the dome of the Sydney Olympic stadium is that they are made of polycarbonate plates.

Interesting Questions

- What were the first plastic materials produced from?
- What are materials that expand when heated?
- Which material is often used as an alternative to glass?
- What parts of airplanes can be made of plastics?
- What is difference between reuse and recycle?

Real Tales

The inventions of modern times are comprehensive and predictable, often based on group work. Talking about the life of Leo Hendrick Baekeland, who belongs to a period of inventions based more on coincidences and personal skills, will be the best guide to his progress towards becoming the father of plastic.

Baekeland, who dreamed of running away from home and wandering the seas in his childhood, was interested in geography, and then managed to photograph the places he travelled in his youth, met the science of chemistry through photographic films. In the evenings, he started attending chemistry classes at Ghent Technical School. When he was 17 years old, he entered Ghent University with a scholarship, and at the age of 21 he received the title of doctor with the degree of "Maxima cum laude" (highest honors). After teaching at the teachers' college for a while, he became a professor at Ghent University at the age of 26 and taught at the same university until 1889. In 1899, he won a scholarship and travelled to the USA to conduct research on the chemistry of photography. He *made commercial use of his work on photographic film and by the time he was 36 years old, he was a very wealthy man. After this date, he was able to devote himself to the work on resins, which he really wanted to do. In 1906, when Baekeland started to work on this subject, the most widely used natural resin was shellac obtained from a small insect species. It was the main ingredient in yellow varnish, lacquers, and many other everyday necessities. However, like all other natural resins, it softened easily. It became difficult to use under pressure and heat. Baekeland began work to produce a substitute for shellac. Before him, other researchers had also made attempts in this field. For example, Adolf Baker had noticed in 1871 that hydrogenated alcohol and phenols influenced each other. Strange things happened when these substances were mixed. For example, when heated, the mixture would boil, foam, sizzle, and scatter molten particles into the environment. When the boiling subsided, what was left was a perforated grey mass that was impossible to work with. It was only in 1909 that he finally mixed phenol and formaldehyde and found Bakelite.*

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CHAPTER 3: BIOPLASTICS

Ulku Sayin, Onder Alici, Yasemin Oztekin,
Giulia Fredi, Alessandro Pegoretti

3.1.Definition and Classification of Bioplastics

Ulku Sayin, Yasemin Oztekin

Polymers are molecules with repeated monomeric components, and plastics are synthetic materials manufactured from high-molecular-weight organic polymers that can be softly molded and then hardened. The two main categories of plastics are conventional plastics and bioplastics. Conventional plastics are petroleum-derived products made from fossil fuels. Sometimes, the meaning of the word **"bioplastic"** can be confused. According to European Bioplastics, bioplastic is a general term given to plastics that are of bio-based origin, biodegradable, or have both features. On the other hand, **"bio-based"** and **"biodegradable"** terms do have not the same meaning; they cannot be used interchangeably. Consequently, bioplastics are not a single class of materials, but rather a vast variety of materials with varying characteristics and uses.

Figure 3.1 depicts the categorization system based on the biodegradability and composition of plastic materials that can be divided into two main groups: bioplastics and conventional plastics (European Bioplastics, 2023a). The quadrants of the system are as follows: **i)** bio-based or partly bio-based non-biodegradable bioplastics, **ii)** bio-based and biodegradable bioplastics, **iii)** fossil-based and biodegradable bioplastics, **iv)** fossil-based and non-biodegradable conventional plastics.

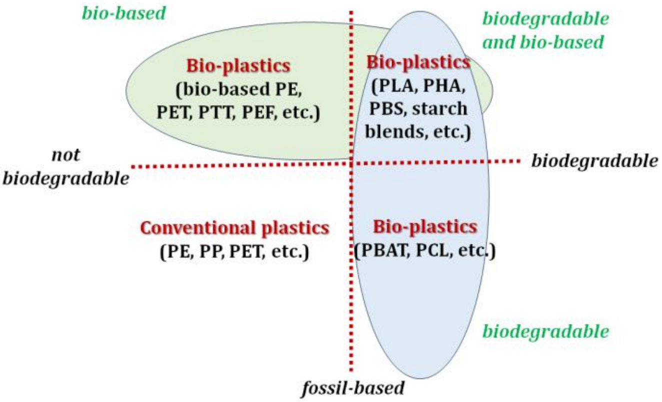

Figure 3.1. The classification system for plastics mainly divides them into bioplastics and conventional plastics (European Bioplastics, 2023a).

Based on their fundamental chemical composition, bioplastics can be categorized as durable or biodegradable polymers. The prefix 'bio-' is sometimes used on bioplastics, regardless of their origin, to indicate the bio functionality of the material (usually biodegradability or biocompatibility) (bio-based) (Kabasci, 2014).

Bio-based plastics are either entirely or partly generated from biomass. Organic biomass can consist of corn oil, orange peel, grass, starch, and plants. It means that bio-based polymers are derived from natural or organic sources (corn, potato, tapioca, rice, or wheat starch, etc.) and oils (palm seed, linseed, soybean, etc.) or fermentation products such as polylactic acid (PLA), polyhydroxyalkanoates (PHA), and polyhydroxybutyrate (PHB). As a general phrase, there are two types of bio-based plastics; **i)** bio-based and biodegradable, which are often used for single-use items, **ii)** bio-based and durable, which are utilized for long-term items. Nonetheless, not all bio-based polymers are biodegradable, and not all biodegradable plastics are bio-based (Bajpai, 2019).

Biodegradable bioplastics can decompose into natural components (such as water, CO_2 and/or CH_4, new biomass, and mineral salts) under specified environmental circumstances by microorganisms during composting or anaerobic digestion without leaving toxic byproducts and then merge innocuously with the soil. In several international standards, the biodegradation process requirements of test procedures and methodologies for analyzing ultimate decomposition have been outlined. Under these standards, polycaprolactone (PCL) and poly(butylene adipate terephthalate) (PBAT), both derived from fossil fuels, meet biodegradability criteria (Kabasci, 2014).

Compostable plastics are a subcategory of biodegradable plastics and are intended to decompose in an environment where conditions are carefully managed. They decompose quickly (~ 80-90 days) and do not create any toxic byproducts that worsen the compost.

Biodegradable plastics provide new, environmentally friendly solutions for waste disposal, such as anaerobic digestion and composting. While some petrol-based plastics are also biodegradable, bio-based biodegradable plastics are considered environmentally benign as they are generated from renewable resources (Filiciotto and Rothenberg, 2021).

3.2.The Usage and Importance of Bioplastics

Ulku Sayin, Yasemin Oztekin

Plastics have been an integral part of numerous industries, from building and farming to healthcare and beyond, ever since they have been first introduced to consumers. On the other hand, the implementation of a circular plastics economy is crucial for the reduction of plastic pollution on a worldwide scale. Recycling is the most desired or conventional end-of-life solution for plastics (recyclable plastics). While recycling is an option, a lot of plastics are still thrown out in the wrong places or end up in the environment. As an example, an estimated more than 1 trillion plastic bags are manufactured annually on a worldwide scale, with a normal average functional life of just a few minutes and a major portion of them becoming trash. Plastic waste can remain in ecosystems for several hundred to thousands of years and turn into dangerous microplastics, that threaten both human and animal health. In reality, plastics are a serious hazard on both land and sea habitats. Therefore, the need to find “green materials” to reduce pollution is urgent. In this sense, bioplastics have recently shown great promise as a good alternative and is becoming a rapidly expanding market segment within the plastics industry (Ferreira-Filipe et al., 2021). Due to their renewable and/or biodegradable nature, they can help in the reduction of fossil fuel use, promote sustainability efforts, and offer businesses the opportunity to diversify their raw materials.

As with other plastics, bioplastics find use in a wide range of industries, including packaging, farming, medicine, the car industry, consumer electronics, catering products, textiles, toys, 3D printing, and more. Additionally, biodegradable plastics reduce the quantity of waste transported to landfills. As a further step toward a more sustainable and environmentally friendly bioeconomy, the use of biodegradable plastics is recommended in some applications, such as soil cover films, carrier bags and disposable packaging (Di Bartolo et al., 2021; European Bioplastics, 2023b).

Bioplastics will take a step forward as new uses and processes are discovered in the plastics industry. Currently, less than 1% of the over 390 million tons of plastic produced each year consists of bioplastics. European Bioplastics and the nova-Institute predict global bioplastics production will increase from 2.23 million tons in 2022 to 6.3 million tons in 2027 (European Bioplastics, 2023c).

It would be worth mentioning Polylactic acid (PLA), produced by fermenting plant starches, as a good example of how bioplastics are important and useful. It is a biodegradable bioplastic derived by chemical polymerization of the bio-based monomer lactic acid and is one of the most widely used bioplastics on the market. Widespread usage of PLA is available in the form of disposable cups, often labeled as “compostable in industrial facilities.” In many different industries, including food packaging, textiles, engineering plastics, biomedical equipment, and many more, this thermoplastic polyester is used because it is made from renewable resources like maize and sugar cane. Compared to other biopolymers, the production of PLA offers several benefits, including eco-friendly, biodegradable, recyclable, compostable, and even biocompatible. Additionally, carbon dioxide is consumed during PLA manufacturing (Farah et al., 2016). The food sector often uses PLA to avoid damaging perishable foods during transportation. On the other hand, it is exceedingly brittle and incompatible with most packaging fabrication techniques. Therefore, it needs to be strengthened with additives. Due to its biocompatibility, PLA an excellent material for biodegradable medical implants.

In summary, it can be said that bioplastics are eco- friendly and innovative materials of the 21st century and are of great importance for the future of our planet. Bioplastics offer numerous benefits in the search for new sustainable material solutions (sourcing, production, and consumption). Therefore, the production of bioplastics has been a priority for many industries for the past four decades.

3.3.Sources and Production Methods of Bioplastics

Onder Alici, Yasemin Oztekin

Bioplastics are synthetic materials generated from renewable biomass sources such as straw, oils, corn starch, woodchips, sawdust, recycled food waste, plant fats, etc. Although several bioplastics are chemically fabricated from lipids (from animals or plants), sugar derivatives, or biologically obtained by the fermentation of molecules like sugars or lipids, the others are generated by reacting with natural biopolymers like polysaccharides and proteins (such as soy protein, gluten, and gelatin). On the contrary, fossil-fuel plastics are produced from natural gas or petroleum (Wikipedia, Bioplastic, 2023).

Based on the source of the raw materials and the corresponding polymer production technology, bioplastic production methods can be divided into four major groups (Figure 3.2) (Song et al., 2011).

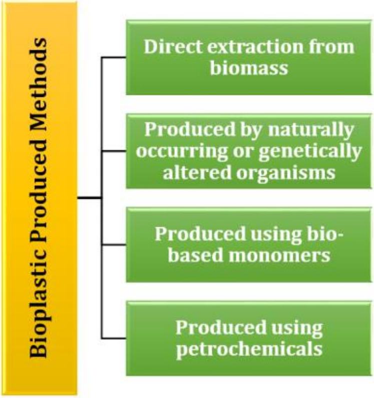

Figure 3.2. Schematic representation of "Bioplastic Produced Methods"

3.3.1.Direct extraction from biomass

Biomass extraction from naturally occurring biopolymers such as proteins and polysaccharides (starch, cellulose, and gluten, etc.) can be used to produce bioplastics. As an example, lignocellulose biomass and starch are being used in industrial settings more frequently, because of their low cost, abundance, and renewable nature (Imre et al., 2019). Material coating, blending, nanoparticle additives, and other chemical or physical modifications are used to overcome poor material properties and usage limitations (Bilo et al., 2018).

3.3.2. Produced by naturally occurring or genetically altered organisms

Certain microorganisms can synthesize aliphatic polyesters, which serve as energy storage materials in cells. These polyesters are then harvested and produced commercially using bioengineering techniques. Polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), polyhydroxyhexanoate (PHH), and their copolymers are all referred as polyhydroxyalkanoates (PHAs) (Chen, 2005). Numerous bacteria, including alcaligenes, eutrophus, and cyanobacteria, can produce polyhydroxyalkanoates. Based on PHA synthesis and accumulation mechanisms, PHA-producing bacteria can be broadly divided into two groups: i) bacteria that need nutrient limitation for PHA biosynthesis from a carbon source (such as oxygen, nitrogen, and phosphorous), and ii) bacteria that can synthesize and accumulate PHA without nutrient limitation (Albuquerque and Malafaia, 2018). There are approximately 250 different species of naturally occurring PHA-producing bacteria. However, only a small number of bacteria, including *Cupriavidus necator*, *Pseudomonas oleovorans*, *Bacillus megaterium*, and *Alcaligenes latus*, were adopted for industrial PHA production (Tsang et al., 2019).

3.3.3.Produced using bio-based monomers

PLA is one of the most widely used and commercially available bioplastics in this group. In a more recent development, bio-ethanol made from sugar was also used to create polyethylene, a non-biodegradable polymer. Another bio-based compound is polyglycolic acid (PGA). Also, with the help of metal salt catalysts at low concentrations, ring-opening polymerization can be used to create PGA, a biodegradable aliphatic polyester, from glycolide (Yamane et al., 2014). Time, temperature, the concentration of the catalyst, and chain transfer agents, can all affect molar mass of the PGA polymer (Hill, 2005).

3.3.4.Produced using petrochemicals

Bioplastics made from petrochemical resources are frequently combined with cellulose or starch rather than being used on their own in packaging because they are significantly more expensive than standard petrochemical plastics (Alashwal et al., 2020). Polymers, which include polyvinyl alcohol (PVOH), aromatic co-polyesters, and aliphatic polyesters, are made from petrochemical monomers and have weak bonds that make them susceptible to enzymatic attack and biodegradation. PVOH has good biocompatibility, hydrophilicity, and biodegradability. It can be produced from the polymerization of vinyl acetate obtained by hydrolyzing polyvinyl acetate (PVAC).

3.4.Formation Mechanisms of Bioplastics

Onder Alici, Yasemin Oztekin

Bioplastics are derived from natural or synthetic sources, such as polysaccharides, proteins, sugars, and lipids. Synthetic versions of bioplastics can be obtained through a wide variety of formation mechanisms. The most well-known of this formation mechanism is the esterification reaction. Monomers formed by fermenting starch or sugar are used in making bio-polyester (Bruder, 2015). Polyesters are polymers in which ester bonds are used to bind the component monomers. Many synthetic polyesters can be broken down through biodegradation, and these ester linkages are typically simple to hydrolyze (Ashter, 2016). Figure 3.3 depicts the polyester's generalized structure.

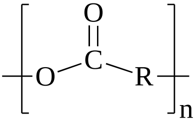

Figure 3.3. Polyester's generalized structure

Among the polyester compounds, the most widely known bioplastic is polylactic acid. The process of synthesizing polylactic acid begins with the production of lactic acid and ends with its polymerization, which is the formation of lactides that serve as an intermediate step. The production of polylactic acid involves the use of two main monomers. These are lactide, which is a cyclic diester, and lactic acid (Figure 3.4).

Lactic Acid Lactide

Figure 3.4. Generalized structures of Lactic acid and Lactide

Usually, fermented plant starches like those from corn, cassava, sugarcane, or sugar beet pulp are used to make these monomers. The general schema for polylactic acid synthesis was presented in Figure 3.5.

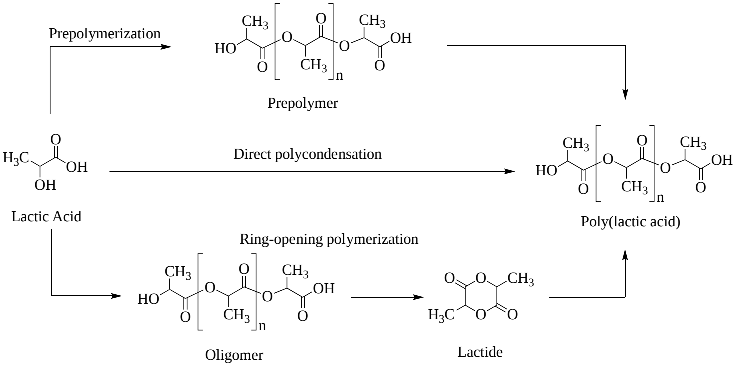

Figure 3.5. Schema of Polylactic acid polymerization (Wong et al., 2020).

The synthesis of PLA can be accomplished through the direct condensation of lactic acid monomers (Wikipedia, Polylactic acid, 2023). Direct condensation calls for longer reaction times and the use of a solvent. It is possible to obtain the final polymer as a low or medium-molecular-weight product (Singhvi and Gokhale, 2013). Also, ring-opening polymerization of lactide with different metal catalysts in solution or as a suspension is the most popular method of synthesizing PLA. L-lactide, D-lactide, or meso-lactide are produced when low molecular weight

PLA is depolymerized under reduced pressure. Depending on the initiator used, the ring-opening polymerization of lactide can be accomplished in melt or solution by cationic, anionic, or coordination mechanisms. Stannous octoate, Sn(Oct)$_2$, shown in Figure 3.6 is the most widely regarded active initiator to produce L-lactide by ring-opening polymerization, and it has a low degree of racemization at high temperatures (Figure 3.7) (Singhvi and Gokhale, 2013).

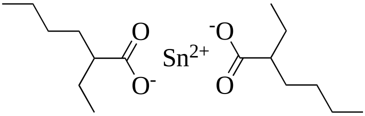

Figure 3.6. General representation of Sn(Oct)$_2$

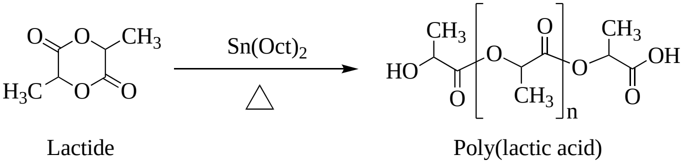

Figure 3.7. Schema of ring-opening polymerization for polylactic acid

Also, transition metals like tin, aluminum, lead, zinc, bismuth, and yttrium catalyze the reaction (Agrawal and Bhalla, 2003).

Another important biodegradable polymer is polyglycolic acid (PGA). Condensation of glycolic acid using a dehydrating reaction is the easiest procedure for synthesizing PGA. However, PGA with a sufficiently high molecular weight cannot be synthesized with this simple method. The ring-opening polymerization method of glycolide is used to synthesize high molecular weight PGA (Figure 3.8) (Yamane et al., 2014).

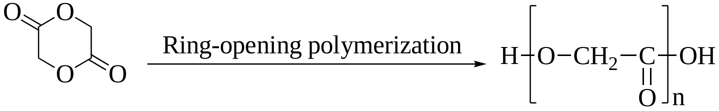

Figure 3.8. Schema of ring-opening polymerization for PGA.

Materials containing PGA are resistant to many organic solvents but are more susceptible to hydrolysis (Song et al., 2011). Due to these properties, materials containing PGA are mostly used in medical applications (Yamane et al., 2014).

3.5.Recycling Mechanism of Bioplastics

Giulia Fredi, Alessandro Pegoretti

Substituting traditional plastics with bioplastics, i.e., plastics that are bioderived and/or biodegradable, it is not sufficient to definitely fix the plastics waste problem. To enhance the sustainability of biopolymers throughout their entire life cycle, increased bioplastics production must be supplemented by the adoption of efficient methods for handling biopolymers products at the end of their life. Among these methods, recycling, and particularly mechanical recycling, must be given prominence because it allows for the reduction of emissions, the carbon footprint, and the consumption of raw materials, as many life cycle assessments (LCA) studies have shown (Vu et al., 2020; Beltran et al., 2021). This is essential for all plastic items, including bioderived and biodegradable polymers.

3.5.1.Benefits and challenges of bioplastics recycling

Plastics’ life cycle, regardless of origin or degradability, is ecologically sustainable only if disposal options include recycling. Although everyone agrees that recycling non-biodegradable plastics, regardless of origin, is convenient, the same cannot be said for biodegradable polymers, for which the only appropriate disposal option is frequently viewed as the biodegradation. However, most biodegradable biopolymers (e.g., PLA and PHAs) degrade slowly ambient conditions, which may severely limit the theoretical benefits of using bioplastics to prevent pollution (Niaounakis, 2019). Furthermore, the biodegradation of plastics can result in uncontrolled methane emissions, which has a harmful effect on the environment (Niaounakis, 2019). Commercial bioplastics must be biodegraded in industrial composting plants, but this should be viewed as the very last life cycle step, following numerous steps of reusing and recycling. T the disposal of bioplastics results in the waste of precious bioderived compounds and natural resources (e.g., lactic acid for PLA). In this view, chemical recycling can convert waste bioplastics into alternative raw material for monomers and intermediates, thus conserving primary resources and further reducing the environmental impact of bioplastics (Niaounakis, 2019).

Additionally, whereas bio-based non-biodegradable polymers like bioPET or bioPE may be blended with their petroleum-derived equivalents at their end of life and recycled in the same facilities, this is not necessarily the case with biodegradable biopolymers (Soroudi and Jakubowicz, 2013). For instance, the existing plastic bottle recycling market, which mostly deals with PET and high-density polyethylene (HDPE), has well-established operating methods, contented clients, raw resources, and shareholders. If additional materials are added to the mix of materials now used, all these conditions must also be met for those new materials (Cornell, 2007). The introduction of biodegradable bioplastics, particularly those used for packaging, into the plastics recycling and green waste composting streams might raise sorting costs, reduce yield, and lower the processability and quality of the recycled or composted output (Soroudi and Jakubowicz, 2013). On the other hand, establishing separate recycling streams would be contingent on gathering a sufficient amount of bioplastics trash, creating technologically feasible, efficient, effective, and affordable recovery technologies, and creating end markets for post-consumer bio-based commodities (Cornell, 2007).

The market for bioplastics is projected to expand in the coming years, thus it will likely be necessary to tackle the issue of recycling both biodegradable and non-biodegradable bioplastics and to research the most efficient recycling paths for both over the long term.

3.5.2. End-of-life pathways for bioplastics and recycling routes

Depending on the product, its market share, and the available infrastructure for collecting and processing it after use, the optimum end-of-life choice will vary. According to the European Directive on Waste Management (Directive (EU) 2008/98/EC, 2008), waste should be handled in accordance with a precise hierarchy implying a priority ranking in the laws and regulation. This hierarchy foresees prevention and reuse as the preferred options, followed by recycling, energy recovery, and disposal in landfills (Figure 3.9).

Recycling is the second-best waste management strategy after preparing materials for reuse, hence any plastic material's life cycle may only be considered truly sustainable if recycling is included among the disposal alternatives. Although recycling non-biodegradable plastics, whether they are bioderived or not, is universally recognized as convenient, biodegradation is frequently viewed as the only acceptable end-of-life choice for biodegradable plastics. However, because they have been manufactured to disintegrate under specific settings, such as in composting facilities, the majority of commercial biodegradable bioplastics decompose slowly under ambient conditions, even in the presence of microorganisms, as they have been designed to degrade in specific conditions, for example in composting plants (Niaounakis, 2019).

Figure 3.9. Hierarchy of waste handling according to the European Directive on Waste Management (Reprinted from (European commission, 2020))

Despite the fact that biodegradation can be thought of as a recycling alternative and is occasionally referred to as "organic recycling" (Kabasci, 2014), it typically does not attempt to recover plastic components or monomers to be reintroduced into the life cycle of plastic goods. Other recycling solutions, such as mechanical (primary or secondary) and chemical (tertiary) recycling, on the other hand, are specifically designed to do so. Therefore, for instance, biodegradable plastics could be mechanically recycled by primary recycling, in which the recycled plastic serves the same purpose as the virgin plastic, provided that the material quality is high, or by secondary recycling, in which the recycled plastic can be used for less-demanding applications (Dorigato, 2021). When the material quality falls below a certain level, bioplastics may be then chemically recycled to extract useful molecules that could be utilized as the basis for new polymers or other valuable compounds. At last, bioplastics waste with very poor material quality may be processed by biodegradation (Figure 3.10). Hence, in order to optimize the environmental advantages of these materials, all viable recycling options should be investigated rather than making a preliminary assumption that biodegradation is always the optimum end-of-life option for biodegradable plastic waste.

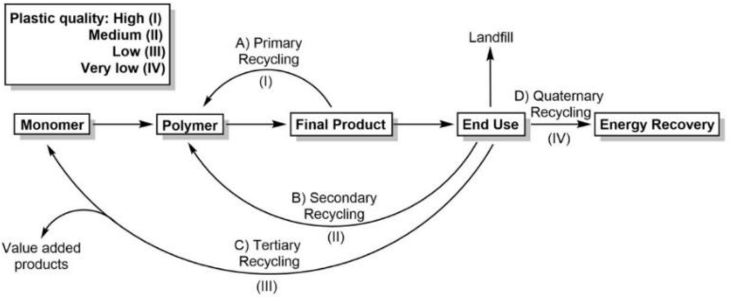

Figure 3.10. Quality of plastic material associated with the various end-of-life options for plastics waste.
(reprinted with permission from Lamberti et al., 2020)

The possible end of life pathways for non-biodegradable and biodegradable bioplastics waste are displayed in Figure 3.11. All disposal pathways start with the identification and sorting of the bioplastic types, after which the different waste streams can be directed towards **i)** recycling through mechanical, chemical, or enzymatic (only for biodegradable plastics) techniques, **ii)** biodegradation, **iii)** energy recovery, or **iv)** landfilling.

The discussion on the end-of-life options for bioplastics will continue in Subchapter 4.5, with a more detailed focus on the recycling and disposal pathways of biodegradable bioplastics.

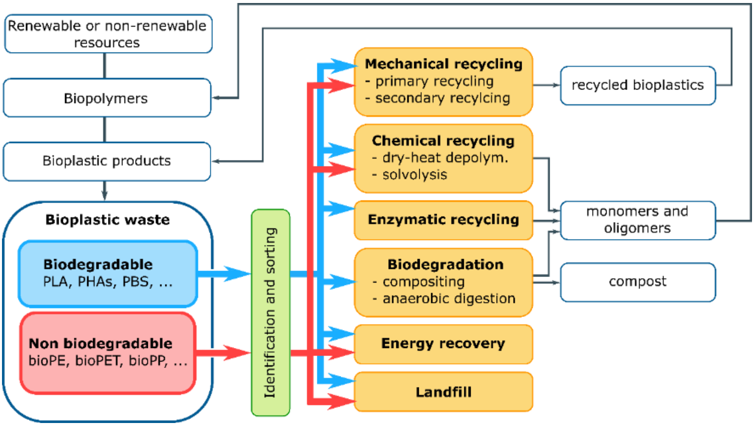

Figure 3.11. End-of-life routes for biodegradable and non-biodegradable bioplastic waste (reprinted from Fredi and Dorigato, 2021).

3.6.Daily Examples of Bioplastics

Ulku Sayin, Yasemin Oztekin

Bioplastics offer many benefits over plastics made from petroleum, as they are renewable and environmentally friendly. That’s why the use of bioplastics has significantly increased during the previous ten years. Packaging, food services, agriculture & horticulture, building & construction, the consumer durables industry, medical equipment, automotive and aerospace, and cosmetics are just some of the applications of bioplastics that are now in use (European Bioplastics, 2023b).

Bioplastics have significantly displaced conventional plastics in the packaging sector. Packaging is the most common use of plastics, particularly in the food industry. Since the majority of packing materials are composed of non-renewable and non-biodegradable synthetic plastics, packaging trash ranks first in landfills. The use of synthetic polymers for packaging, particularly in the food industry, has also been linked to several health problems. Because of this, firms in the packaging industry are required to switch to using bio-based and biodegradable or compostable materials (Pilla, 2011). In contrast to standard synthetic polymers derived from petroleum, biopackaging materials derived from sustainable raw resources such as polysaccharides, proteins, and lipids or their mixtures may be recycled and reutilized. Moreover, biopolymer films and coatings may operate as barriers and complement other forms of packaging by preventing food from spoiling and extending its shelf life. Shopping bags, garbage bags, agricultural foils, horticultural products, textiles, and toys are just a few examples of the packaging industry’s wide applications of bioplastics. Starch and proteins have been utilized as biodegradable films and coatings for packaging purposes, safeguarding fruits, and nuts from damage, minimizing fruit shrinkage, and preventing rancidity. Since the biodegradable plastic PLA has the greater mechanical strength and heat-resistance of all biopolymers, its most common use has been in the manufacture of food packaging, including as food trays, tableware (including plates and cutlery), water bottles, candy wrappers, cups, and so on (Bajpai, 2019).

Bioplastics and biocomposites play an essential role in the development of innovative materials for use in a broad range of biomedical applications (implants, tissue engineering, drug delivery systems, etc.), because of their biobased, biodegradable, and biocompatible properties (the most critical aspect for biomedical applications). Bioplastics and/or bionanocomposites are also used in cancer treatment and diagnostics, gene vectors, biosensors, and dental applications like dental implants, all of which are very important subfields of biomedical engineering (Pilla, 2011). Medical teams are increasingly using nontoxic biodegradable bioplastics sutures, often known as stitches, in hospitals and operations. They are simple to sterilize, durable and stay in place until the tissue heals, at which point they are destroyed by the body, leaving no trace. Bioplastics are also being utilized to make instruments for bone repair and reconstruction, such as pins, tacks, and screws.

Bioplastics have replaced petroleum-based plastics in the automotive sector over the last few decades because of technological advances, increasing greenhouse gas emissions, and a heightened emphasis on environmental sustainability and vehicle life management. Biocomposites produced by strengthening plastics with fibers (natural fiber-reinforced bioplastics) derived from renewable resources (such as cellulose, soy, hemp, and flax) are the most extensively used bioplastics in the automotive industry. Bio-based polypropylene (Bio-PP) has started to replace polypropylene in a variety of applications (bumpers, spoilers, dashboards, air conditioning, battery covers, air ducts, etc.). PLA is particularly appropriate for inside-the-vehicle parts (mats, carpeting, and upholstery, etc.), and Bio-polyamides (Bio-PA) due to their good mechanical properties may be utilized in quick connectors, pneumatic brake noses, fuel lines, flexible tubing, and friction parts (Pilla, 2011; Barrett, 2019).

In the consumer electronics industry, a growing number of bioplastic goods are launched, including touchscreen computer casings, loudspeakers, keyboard parts, mobile casings, vacuum cleaners, and laptop mice (Pilla, 2011).

The agricultural industry is gradually accepting the use of bio-based plastics in the mulching process as a better alternative to polymers made from fossil fuels.

Highlights

- “Bio-based” and “Biodegradable” terms do have not the same meaning; they cannot be used interchangeably.
- Biodegradable bioplastics can break down into natural substances by the action of microorganisms under certain environmental conditions. This decomposition process does not produce any harmful byproducts and the bioplastics may safely integrate with the soil.
- Plastics have played a crucial role in several sectors, including construction, agriculture, healthcare, and more, since its first introduction to consumers.

Interesting Questions

- Who discovered the first bioplastic?
- What is the most used bioplastic in daily life?
- What is the best-known formation mechanism for bioplastics?
- Are bioplastics important? Why?

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CHAPTER 4: PROPERTIES OF BIODEGRADABLE PLASTICS

Aniello Gervasio, Gennaro Velotto
Giulia Fredi, Alessandro Pegoretti

4.1.Chemical Structures

Aniello Gervasio, Gennaro Velotto

The International Union of Pure and Applied Chemistry (IUPAC) defines plastics as “polymeric materials that may contain substances designed to improve their properties or reduce their cost”. From a chemical point of view, the result is obtained by linking a series of chemical units called monomers that, compressively, can determine a more or less complex chain. It’s possible to consider **i) homopolymers** if there is a single monomer, **ii) copolymers** if the polymer is obtained from two or more different monomers and **iii) polymer alloys** if the material is obtained by mixing two monomers that polymerise without combining chemically.

Plastic can be considered as an organic compound. In turn, an organic compound, to be defined in this way, is composed of carbon (C) atoms within its structure. In the case of plastics formulation these carbon atoms bind - through covalent bonds - to atoms of hydrogen (H), oxygen (O) and nitrogen (N), but not only. These molecules bond resulting in the formation of long chains referred to as macromolecules. Macromolecules can be longer or shorter and can form polymers. The polymers obtained will be materials characterized by their versatility of use and easiness of processing/modelling. Various substances (also called “fillers”) could be added to the normal polymer base, depending on the application. These substances can give specific characteristics to the plastic material referring to desired properties of workability, appearance, and strength.

Plastics, unlike other organic substances, are not found in nature and must be artificially synthesized from natural resources such as gas, oil, and its derivatives. Therefore, production begins with the extraction/processing of fossil fuels and their polymers: propylene, ethylene, butadiene, and styrene. In particular, oil and gas are hydrocarbons, i.e., organic polymeric substances composed exclusively of carbon and hydrogen. In order to realize the final product, i.e., plastic, it is essential and necessary to break them down into their basic elements and this process of decomposition can be achieved by “cracking” whereby the long chains of hydrocarbons are broken.

In summary, there are two main types of processes around which “plastic chemistry” revolves: polymerization and polycondensation. Polymerization occurs due to a combination of heat, pressure, and enzymatic catalyzing reactions, while polycondensation consists of dissolving the two substances with different reactive functions in two immiscible liquids; if the two solutions are mixed by agitation, the reaction occurs at the interface (interfacial p.) of the particles of the dispersed phase and the polymer, if insoluble, precipitates in the form of granules. Furthermore, in the former case, monomers such as ethylene and propylene are bound together while remaining intact; in the latter, the monomers are not simply added together, but “condensed” by removing water or methane molecules.

At the end of these chemical processes, various types of plastics can be recognized, each obtained through different processes and different chemical elements/compounds:

- Polyurethanes - PU: Chemical reaction between di-isocyanates (with 2 or more -N=C=O groups in the molecule) and polyols (with 2 or more -OH hydroxyl groups) in the presence of suitable catalysts.
- Polytetrafluoroethylene - PTFE (Teflon): Polymerization of tetrafluoroethylene
- Polyacetals - POM: Polymerization of formic aldehyde
- Polyamide - PA: Reaction between diamines and dibasic acids or between lactams and amino acids
- Polybutilenterphthalate - PBT: Condensation of terephthalic acid with butylene glycol
- Polycarbonate - PC: Reaction of bisphenol and phosgene
- Polyphenylenoxide - PPO: Aromatic polyether polycondensation of 2,6-methylphenol
- Polyethylene or Polythylene - PE: Polymerization of ethylene
- Polyphenylensulphide - PPS: Treatment of paradichloro-benzene with sodium sulphide in the presence of solvents
- Polyethylenterphthalate - PET: Condensation of terephthalic acid with glycolethylene

- Polyvinylidencloride - PVDC: Polymerization of polyvinylidene chloride
- Polymethylmetacrylate - PMMA: Polymerization of methacrylic acid
- Polyvinylidenchloride chloride - CPVDC: Chlorination of polyvinyl chloride
- Polypropylene - PP: Polymerization of propylene
- Polystyrene or Polystyrylene - PS: Polymerization of styrene
- Expanded Polystyrene - EPS: Polymerization of styrene in the presence of a blowing agent.
- Polyvinylacetates - PVA: Polymerization of vinyl acetate
- Polyvinyl Chloride - PVC: Polymerization of vinyl chloride

Unlike the chemistry present in the generic formulation of plastics described above, when it comes to biodegradable plastics it’s necessary to follow a different direction and introduce the concept of “Green Chemistry”.

“Green or Sustainable Chemistry” is an idea of chemistry that aims to steer the approach to the chemical industry along sustainable paths. Sustainable development requires the conversion of old chemical methods into new clean processes and the design of new eco-friendly products. Major government environmental agencies, industry and the chemical world in general are active in identifying precise strategies to prevent pollution. In September 2015, more than 150 international leaders met at the United Nations to contribute to global development, promote human well-being and protect the environment. The community of states endorsed the 2030 Agenda for Sustainable Development, the essential elements of which are the 17 Sustainable Development Goals (SDGs) and 169 sub-goals, aimed at ending poverty, combating inequality and social and economic development. In addition, these are linked with fundamental aspects for sustainable development such as: ensuring production and consumption patterns (goal 12); ensuring sustainable management of the planet's water (goals 6 and 14); protecting, restoring, and promoting sustainable use of the earth's ecosystem (goal 15); promoting sustainable industrialization and innovation (goal 9). All the goals have to take place by the year 2030. To achieve all of them, it was necessary to find materials that had the same properties as conventional plastics but were not harmful to the environment: bioplastics.

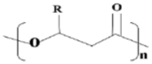
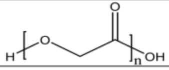
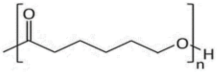
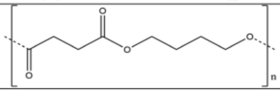
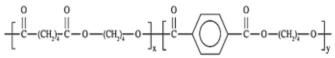
Consequently, bioplastics can be considered as environmentally sustainable and less polluting materials as they are not derived from oil refining, but from renewable energy sources such as biomass. The term biomass is not synonymous with biodegradable but identifies a material that is degraded through the action of microorganisms (bacteria, fungi and/or moulds). Hence, two categories can be distinguished: **biodegradable bioplastics**, if are able to degrade independently in the environment by natural organisms, or **biocompostable**, if it’s necessary “an incentive” for degradation by the addition of microorganisms (microbial consortium), and then used as fertilizers. In general, bioplastics can be considered as synthetic polymers and is possible to talk about biopolymers. In particular, these are condensation polymers made from the union of two monomers, such as a carboxylic acid and an alcohol (or an amine), with the elimination of H_2O. This characteristic makes them more easily hydrolyzed to their original status by biological agents such as enzymes (and consequently the cells containing them). To achieve the natural utilization by biological agents, bioplastics must contain molecules that are metabolizable, or at least absorbable, by cells. For example, polyethylene terephthalate (PET), although a 100% recyclable condensation polymer, is not biodegradable because the monomer characterizing its structure cannot be metabolized by cells. This implies that it cannot be disposed of by the environment unless recycled to produce new plastic. The purpose of the formulation of bioplastics and the presence of specific chemical characteristics is precisely to achieve easy disposal and possible use of the material by other organisms. This makes it possible both to provide new resources for foodstuffs and at the same time to reduce the environmental pollution normally observed with non-biodegradable plastics. In fact, “non-degradable” plastics need decades or even centuries to degrade (Kjeldsen et al., 2018) because the chemical structure cannot be adequately altered by naturally occurring microorganisms, water, or carbon dioxide (Tokiwa et al., 2009; Babu et al., 2013).

In the context of biodegradable plastics, depending on the chemical composition, it’s possible to identify different types of end products, among which polylactic acid (PLA), for example, can be observed. PLA is derived from the polymerization of lactic acid ($C_3H_6O_3$) and can be easily obtained from organisms such as lactobacilli by exploiting the lactic fermentation process. Lactic acid contributes itself well to the synthesis of homopolymers as it possesses both a carboxylic group (-COOH) and an alcoholic group (-OH), which can merge by condensation. The process involves the formation of a particular cyclic dimer called lactide, which is broken by an enzyme and heat to compose the polymer.

Analyses of the chemical structures of plastics have revealed that decomposition conditions are governed by the physical and chemical characteristics of the type of plastic being discarded, such as mobility, crystal structure, molecular weight, functional groups, etc. (Muthukumar and Veerappapillai, 2015). For example, high molecular weight, high degree of crystallinity, high hydrophobicity and insolubility in H_2O are some factors that can significantly reduce the degradability of plastics (Muthukumar and Veerappapillai, 2015; Urbanek et al., 2018; Ghatge et al., 2020) Indeed, these are the properties that make petroleum-based plastics polyethene and polypropylene non-biodegradable (Tokiwa et al., 2009; Ghatge et al., 2020)

In the overview of biodegradable structures (biodegradable polymers), some references of bioplastics together with their chemical structure are shown below (Table 4.1).

Table 4.1. Examples of bioplastics and relative chemical structures

Name	Chemical structure	Reference
Polyhydroxyalkanoate (PHA)		Priyadarsh, 2014
Polyglycolic Acid (PGA)		Samantara, 2020
Polycaprolactone (PCL)		Aoki and Saito, 2020
Polybutyl Succinate (PBS)		Xu, 2019
Polybutylene Adipate Terephthalate (PBAT)		Nobrega, 2012

4.2. Chemical Properties

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The reason why plastics are preferred in certain applications over metallic and non-metallic materials is linked with the easiness of processing, cost-effectiveness, colourability, acoustic, thermal, electrical, mechanical (vibration) isolation, corrosion resistance and chemical inertness, as well as their water repellency and inactivity to moulds, fungi, and bacteria. Bioplastics, on the other hand, are important because minimize the use of fossil resources and, at the same time, achieve lower emissions throughout the entire life cycle of the products. These materials also greatly improve resource management and the options available at the end of the life cycle of products made from bioplastics. Therefore, this type of "eco-friendly plastic" allows for a considerable reduction in the number and impact of waste on an ecosystem level, as well as the workload on disposal plants.

With reference to the different examples of bioplastics given in Subchapter 4.1, is possible to emphasize the chemical properties of the mentioned materials.

4.2.1. Polyhydroxyalkanoates - PHA

Polymers synthesized by certain well-known types of bacteria (*Bacillus*, *Rhodococcus*, *Pseudomonas*, etc.) that carry out fermentation processes of sugars or lipids. They are 100% biodegradable and obtained from renewable sources. Due to the great variability of the side chains (-R) and the length of the main chain (m), polyhydroxyalkanoates (PHAs) have highly variable chemical properties ranging from those typical of thermoplastic polymers to those typical of rubbers (elastomers). In an overview, it can be said that depending on the number of carbons (C) in the side alkyl group (-R), they are chemically classified into three classes: *scl*-PHA - short-chain (less than 5 C atoms); *mcl*-PHA - medium-chain (5-14 C atoms) and *lcl*-PHA, long-chain (more than 14 C atoms).

4.2.2. Polyglycolic acid - PGA

Identified according to IUPAC nomenclature as 1,4-Dioxane-2,5-dione. It is a member of the aliphatic linear polyester family and can be obtained by condensation or polymerization. In particular, chemical synthesis can occur by polymerization of glycolic acid, although direct condensation of hydroxycarboxylic acid does not lead to the formation of a high molecular weight polymer. Therefore, it is typically produced by ring-opening polymerization of the cyclic diester known as glycolide using tin (II) octanoate as a catalyst. In this second way, it is possible to obtain the formation of a polymer with a higher molecular weight. Finally, the rough formula is identified as monomer $(C_2H_2O_2)_n$, a molar mass (u) of 58.04 and a density (g/cm^3) of 1.530.

4.2.3. Polycaprolactone - PCL

PCL is a polymer belonging to the family of linear aliphatic polyesters. It is obtained by ring-opening polymerization using stannous octanoate as a catalyst. Its monomer unit is ε-caprolactone ε-CL thus a cyclic monomer with the brute chemical formula $C_6H_{10}O_2$. It dissolves at room temperature when it is in contact with solvents of a different chemical nature such as dimethylacetamide (DMAc), dichloromethane (MC), tetrahydrofuran (THF), chloroform or dimethylsulfoxide (DMSO) depending on the type of application (Nishio and Manley, 1990). The most important characteristic of PCL, from a chemical point of view, is its ability to degrade in a physiological environment. In particular, it is affected by degradation phenomena due to the easy interaction that the aliphatic ester bond, present along the main chain, can have with H_2O molecules. Due to this mechanism, polycaprolactone is regarded as one of the main bioerodible polymers (Ali et al., 1993). The degradation process of PCL is characterized by at least two steps, and in one of these, there is a non-enzymatic bulk hydrolysis of the ester bond autocatalyzed by the carboxyl groups along the main chain (Ali et al., 1993).

4.2.4. Polybutyl succinate - PBS

Polybutylene succinate (PBS) is an aliphatic polyester consisting of butylene succinate units with the brute formula $C_8H_{12}O_4$. PBS can be synthesized by polycondensation of succinic acid and 1,4-butanediol. The synthesis process involves a two-stage bulk polycondensation. The first consists of the esterification of succinic acid with the formation of oligomers and removal of while in the second stage, developed under vacuum, the oligomers formed in the first undergo trans-esterification with obtaining the high molecular weight polymer and removal of excess glycol (Xu and Guo, 2010). For example, it can be obtained biologically by exploiting the fermentation of sugars catalyzed by *Candida Antarctica* (Azim et al., 2006). In order to modify the properties of the final product, copolymers can be obtained by copolymerization with other monomeric units, including adipic acid and terephthalic acid.

4.2.5. Polybutylene adipate terephthalate - PBAT

Polybutylene adipate terephthalate is a copolymer and more precisely a copolyester of 1,4-butanediol esterified with adipic acid and dimethyl terephthalate. This, in fact, appears to be the most suitable combination in terms of excellent properties and good biodegradability. Its overall structure consists of an aliphatic part that is associated with its biodegradability and an aromatic part that provides the rest of the physical/mechanical properties. The mixture of aliphatic and aromatic polyesters also allows the degradation rate to be controlled by varying the compositions of the homopolymers in the copolymer. It is also considered a “random copolymer” in association with the many nuances its chemical structure can have. This structure, having no significant structural order, can be modified by blending processes with other (strong and rigid) biodegradable polymers to produce, for example, bottles. Its production represents a practical, fully biodegradable alternative to low-density polyethylene (LDPE) due to their similarities in flexibility and stretch resistance.

4.3.Physical Properties

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The global biopolymers market is expected to grow from USD 10.7 billion in 2021 to USD 29.7 billion by 2026. The increase in demand for bioplastics and biopolymers is driven by the concern for environmental protection and the possibilities of use. Particularly relevant in this respect is the ongoing analysis of the physical properties of certain biodegradable compounds in order to hypothesize single form uses or possibilities for the production of composite materials obtained from the combination of biodegradable polymers of different natures and syntheses. With reference to physical properties, in this subchapter the properties of some of the most interesting materials previously reported in Subchapter 4.1 and 4.2 will be analyzed and described.

4.3.1. Polyhydroxyalkanoates - PHA

PHAs are generally semi-crystalline thermoplastic polymers, and their physical and mechanical properties are similar to those of other widely used plastics such as propylene and low-density polyethylene. The properties of these polyesters depend on their chemical structure (homopolymer or copolymer) and given the existence of many different monomers; it is possible to obtain end results with different properties. Among the most useful characteristics of PHAs are their biodegradability, biocompatibility, and low water vapour permeability. This makes them very interesting in various sectors such as medical-surgical or food packaging. PHB has some thermal and mechanical properties that are comparable to polymers of fossil origin (e.g., polypropylene), i.e., a high melting point and good tensile strength. However, PHB has some stiffness and brittleness issues (verified by “Young's modulus” or “modulus of elasticity”) due to the formation of large crystals during a re-crystallization that occurs over a certain time interval at room temperature.

4.3.2. Polyglycolic acid - PGA

Polyglycolic acid has a glass transition temperature of 35-40°C and a melting temperature of 225-230°C. This polymer is also characterized by a high degree of crystallinity (around 45-55%), which makes it insoluble in water. (Middleton and Tipton, 1998). The solubility of polyglycolic acid is a special case in that its high molecular weight form is insoluble in almost any commonly used organic solvent (acetone, dichloromethane, chloroform, ethyl acetate and tetrahydrofuran), whereas the low-weight oligomers are characterized by sufficiently different physical properties to be soluble instead. Solvents containing a high number of fluorine atoms, such as 1,1,3,3-hexafluoro-2-propanol and hexafluoroacetone are, however, able to dissolve high-PM polyglycolic acid, allowing the preparation of solutions useful in the preparation of fibres and films (Chen, 2001). PGA fibres are very stiff and have a high Young's modulus value of 7 GPa (Middleton and Tipton, 1998).

4.3.3. Polycaprolactone - PCL

PCL has a longer biodegradation time than the rest of the polymers previously described (approximately two to three years) as suitable enzymes are required, which are currently only present in some organisms such as bacteria or fungi. In addition, it has a relatively low cost and is performant in various applications, bio-assimilable, breathable, hydrophobic, easily pigmented and colored, resistant to grease and moisture, compatible with many materials and possesses a good adhesion capacity to various types of substrates. It has a melting temperature of 59-64°C, a glass transition temperature close to -60°C and possesses a deterioration temperature of approximately 360°C. It appears with an almost crystalline structure and has a tensile strength of 16 MPa and a tensile modulus of 0.4 GPa. Finally, it has excellent flexibility and toughness (at low temperatures) and due to its particularly low softening point can also be used for applications where removable and short-lived plastics are required.

4.3.4. Polybutyl succinate - PBS:

PBS is a semi-crystalline polymer with a degree of crystallinity ranging between 35%-45% with a Young's modulus of 300 - 500 MPa (Xu and Guo, 2010; Gualandi et al., 2012). The melting temperature (T_m) is approximately 130°C and the glass transition temperature (T_g) is in the range of -34°C to -15°C (Zhihua, 2001). Hydrolytic degradation is very slow under physiological conditions (37°C and pH=7.4). In the absence of enzymes, acceleration can be triggered by pH changes and temperature increases (Gualandi et al., 2012). However, the most effective degradation is always obtained by enzymes (Gigli et al., 2012; Gigli et al., 2013; Gigli et al., 2016), which sometimes occurs by exploiting microorganisms such as *Firmicutes* and *Proteobacteria* (Suyama et al., 1998). The product obtained upon primary degradation is succinic acid as described above and is an intermediate in the Krebs cycle. It can therefore theoretically be degraded within the human body in the presence of H_2O and CO_2 (Manavitehrani et al., 2016). An important factor limiting the application of this polymer in the biomedical field is its hydrophobicity, which makes it difficult to interact with cells (Gualandi et al., 2012; Manavitehrani et al., 2016). The low glass transition temperature value allows easy processability using extrusion, injection moulding and thermoforming (Miyata and Masuka, 1998; Papageorgiou, 2005). Finally, the different properties include high productivity comparable to polyolefins, the natural white colour of the raw material, high crystallization speed, high flexibility and strength, good isolation capacity, good adaptability (it can be customized according to the need for use) and it complies with UNI EN 13432 and UNI EN 14995. PBS is less rigid and resistant than PLA while its physical properties are similar to those of polypropylene and polyethylene and can, therefore, be used to create flexible or rigid packaging.

4.3.5. Polybutylene adipate terephthalate - PBAT

Some of the most important properties of PBAT are its high binding properties, good isolation, high flexibility and strength, and versatility in handling. An amorphous thermoplastic state, biodegradability, high flexibility, good thermal stability (up to 230°C), possibility of printing and use in contact with food were also observed. In addition, it has a melting point (DSC) at 10°C/min of 115-125°C, a crystallization point (DSC) at 10°C/min of 60°C with a weight loss of 5% (thermogravimetric analysis) at 20°C/min of 350°C, and a heat distortion temperature (ASTM D6481) at 1.82 MPa with a thickness of 6.4 mm at 55°C, elongation at break of 660% and a flexural strength of 7.6 MPa and flexural modulus of 125 MPa. However, the properties of PBAT are influenced by the composition of the monomers in the structure and their molecular weight.

4.4.Preparation Methods

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According to the European Bioplastics definition, a material to be defined as bioplastic must possess at least one of these characteristics, i.e., be biodegradable or be "biobased" (European Bioplastic, 2016; Figure 4.1). The latter term indicates that the end product is obtained wholly or partially from renewable resources (United States Department of Agriculture, 2006).

When considering the aspect of biodegradation, reference is made to the possibility of the material being transformed through the intervention of microorganisms that convert the material into natural substances that have a low negative impact on the environment (material and process sustainability). It is important to emphasize that biodegradability does not depend on the origin of material, but on its chemical structure (European Bioplastic, 2016).

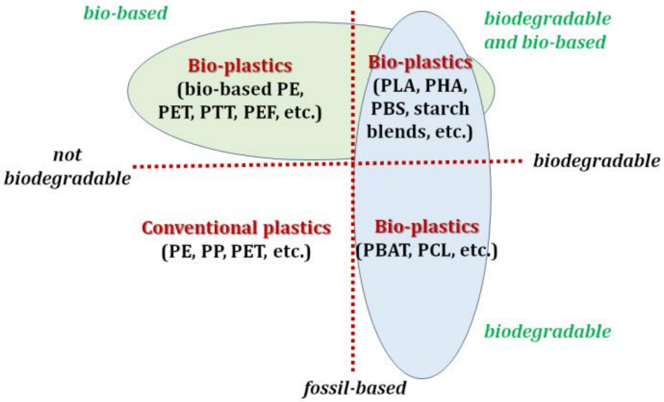

Figure 4.1. Chart edited by European Bioplastic (European Bioplastic, 2016)

The abundance of bioplastics in the market, along with the multitude of those still in the developmental stage, will make waste management much easier, and considering their promising potentials, bioplastics will soon be used in all areas where traditional plastics are used today. In relation to this, the preparation and use encapsulate various advantages including reduced CO_2 impact, lower production cost (for some types), minimal use of fossil resources (oil) and reduction of non-degradable plastic waste that has a significant negative environmental impact. In the context of production as well, the steady growth of the bioplastics market confirms the increasing interest in these innovative materials. From 2010, when 700,000 tonnes of bioplastics were produced, to 1.7 million tonnes in 2015 (Soroudi and Jakubowicz, 2013). Predictions confirm a growth possibility for the coming years (Figure 4.2).

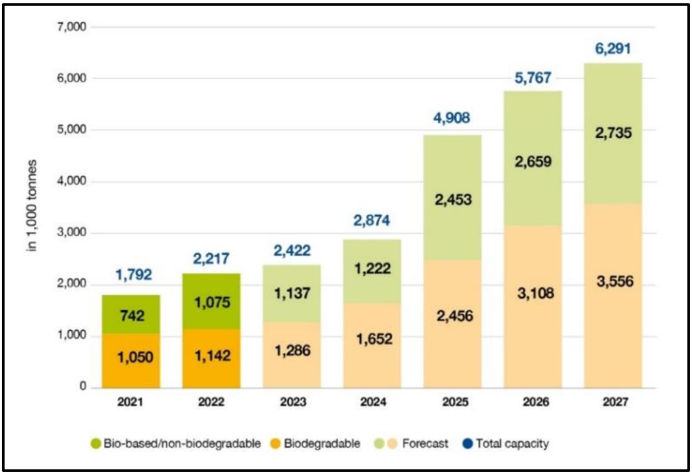

Figure 4.2. Global production capacities of bioplastics (European Bioplastics, 2022)

The above graph (expresses value in 1,000 tonnes) shows the forecast until 2027 according to which approximately 6.2 million tonnes of bioplastics will be produced (estimated value). Furthermore, according to the EU Regulation, by 2030 food packaging and containers must be reusable or recyclable (Gómez-Gast et al., 2022). Therefore, researchers are actively engaged in the development of new biopolymers to finalize this very important achievement.

The production of bioplastics can take place in different ways as given below:

4.4.1. Directly extracted from biomass

Such as polysaccharides (a group of carbohydrates) formed by the repetition of monosaccharides. In nature, there are plants from which they can be extracted as such, e.g., cellulose and starch. These two substances are processed and sometimes mixed with adjuvants to suit different types of uses (Coles et al., 2011).

4.4.2. Obtained from bioderived monomers

Such as polylactic acid (PLA), polyglycolic acid (PGA) and bio-polyethylene. The former originates from the fermentation of biomasses such as maize or sugar cane while the latter originates from the fermentation of biomasses and the opening of the glycolic acid ring by condensation or polymerization reactions. The third is a biomaterial that is being analyzed to replace polyethylene (PET) and it's produced by fermentation of biomasses from ethylene, thus an ethanol derivative (Coles et al., 2011).

4.4.3. Obtained directly from microorganisms

Synthesis processes naturally developed by certain classes of microorganisms are exploited. Useful substances are found in accumulation within a microorganism in the form of granules due to the activation of a natural energy reserve storage mechanism (Coles et al., 2011). This type of polymer is called polyhydroxyalkanoate (PHA).

When it comes to possible applications of produced bioplastics, the largest segment is occupied by packaging. In particular, it is believed that at least 1/3 of the materials produced are used for this purpose. A clear example of this is food packaging, where its use is highest. In particular, PLA is used in rigid packaging while in flexible packaging we can find examples as diverse as packaging made from starch, compostable coffee capsules and compostable ice cream tubs. When it comes to transport and service packaging such as bags, compostable bags have become popular, which can then be given a second life (reuse) when used to dispose of food (wet waste). For a bag to be compostable, it must comply with the European standard EN13432, which defines a close relationship between chemical structure and degradability of the material obtained at the end of the production process.

In the following part, just to give a concrete example, useful protocol for defining how bioplastic production can take place in a laboratory environment (controlled conditions) is shown.

The procedure is outlined below:

i) Safety rules

- Use protective gloves and safety glasses
- Work under the hood

ii) Material

- 25 mL distilled water
- 2.5 g corn starch
- 2.5 g glycerine
- 3 mL of 0.1 M HCl
- 3 mL of NaOH 0.1 M
- Food colouring
- Litmus paper

iii) Procedure

- Weigh 2.5 g of cornstarch and 2.5 g of glycerine into a 100 mL beaker.
- Add 25 mL of H_2O and stir using a glass rod: an opaque milky mixture will be obtained.
- Add 3 mL of 0.1 M HCl and heat for several minutes while stirring on a hot plate. When the mixture starts to heat up, it takes on a uniform, transparent color and then a gel forms.

- Allow the gel obtained to cool for a few minutes, then add a 0.1 M NaOH solution drop by drop until neutralization is checked using litmus paper.
- Add drops of food coloring until the coloring is clearly visible and mix thoroughly.
- Place the resulting mixture in a suitable container (e.g., Petri dish) and dry at room temperature for a few days or in an oven at 100°C for 2 hours.
- Repeat the preparation of the bioplastic without the glycerol and always lay it on a thin layer as in the previous case. The comparison of the properties of the film obtained with and without glycerol is relevant to highlight the plasticizing function of the reagent.
- After drying, the bioplastic films can be gently removed from the substrates used for deposition.

iv) Expected results

The material obtained by using glycerol as a reagent is elastic and deformable, and thus has plastic characteristics, whereas in the second case, the material is rigid and brittle and therefore breaks when subjected to deformation.

4.5.Recycling Mechanisms for Biodegradable Plastics

Giulia Fredi, Alessandro Pegoretti

Biodegradation is not necessarily the best end-of-life option for biodegradable bioplastics. Instead, mechanical, and chemical recycling coan extend the life of the synthesized biopolymer or its renewable monomers, respectively, thus postponing biodegradation and further increasing the sustainability of these materials. However, introducing biodegradable bioplastics into current and well-established recycling streams can raise sorting costs, reduce yield, and lower the processability and quality of recycled output. Additionally, setting up separate recycling streams for bioplastics can be an option, but this depends on gathering sufficient amounts of bioplastic waste, developing efficient recovery technologies, and creating end markets for post-consumer bio-based commodities.

4.5.1. Mechanical recycling

Mechanical recycling is the primary strategy for recovering plastic because it is generally less expensive, involves relatively basic machinery, and has a smaller environmental impact than chemical recycling (Aumnate et al., 2017; Lamberti et al., 2020). Waste collection, screening, and manual or automatic sorting are the first processes in mechanical recycling, which also includes steps like grinding, washing, drying, compounding/extrusion, and granulation (Pacheco-Torgal et al., 2019). Mechanical recycling includes primary and secondary recycling. Primary recycling is a closed-loop technology that can only be used on high-quality plastic trash with a well-known history (Worrell and Reuter, 2014). Conversely, the mechanical treatment of post-consumer plastics is known as secondary recycling. Because of diminished material purity and degradation processes that occur over the product's life, after secondary recycling, the recycled material often has inferior mechanical properties to the virgin product (Lamberti et al., 2020; Dogu et al., 2021).

Despite mechanical recycling being an established recycling approach for standard plastics, it should be used with caution when applied to biodegradable bioplastics. The majority of polymers in this family, such as polylactic acid (PLA), polyhydroxyalkanoates (PHAs), and polyglycolic acid (PGA), are aliphatic polyesters and consequently very thermosensitive (Letcher, 2020). For example, PLA and PGA are prone to heat deterioration, which produces coloring and a loss of mechanical performance. Their high hygroscopicity exacerbates this problem, since absorbed water promotes the hydrolytic breakdown of the molecular chains at high temperatures, thus increasing thermal deterioration. As a result, it is critical to correctly dry these bioplastics before physically treating them. Furthermore, paper contaminants, which might also contain humidity, can impede efficient drying (Kabasci, 2014).

Another concern with PLA is its low T_g (55-60°C), at which the material gets sticky. This property, in conjunction with the poor crystallization rates, makes it challenging to dry and/or crystallize amorphous waste plastic objects such as films. Thermomechanical deterioration during mechanical reprocessing can be prevented in part by using appropriate additives that do not damage the material’s final biodegradability (Beltran et al., 2021). Silk fibroin nanoparticles and functionalized chitosan are two organic fillers that have a nucleating impact on PLA and serve to offset the recyclate's reduction in thermal stability, tensile strength, toughness, and gas barrier performance (Beltran et al., 2021). Similarly, thermoplastic starch (TPS) is susceptible to hydrolysis during use, therefore recycled material should be used for less demanding applications. It is also immiscible with conventional packaging polymers and cannot be co-recycled into high-performance secondary goods (Niaounakis, 2019; Lamberti et al., 2020).

4.5.2. Chemical recycling

Chemical recycling, also known as tertiary recycling, involves the conversion of waste materials into valuable chemicals such as monomers and/or oligomers, which may be reintroduced into the polymer production chain and re-used for polymerization (Niaounakis, 2013). Tertiary recycling of biopolymers is focused on aliphatic polyesters, which are depolymerized in a controlled manner with the goal of conserving primary resources. Unlike mechanical recycling, various chemical recycling procedures may be used on low-quality, heterogeneous, deteriorated, or contaminated plastic trash to turn it into high-added-value chemicals, but it often necessitates greater temperatures and is more energy-consuming.

Chemical recycling can be conducted using dry-heat depolymerization techniques (for example, pyrolysis) or solvolysis procedures (for instance, hydrolysis, alcoholysis) (Piemonte et al., 2013; Vu et al., 2020). PLA may be hydrolyzed to lactic acid with a 95% conversion rate in 2 hours at 160-180°C, where the rate of hydrolysis is proportional to the concentration of polymeric bonds, water, and acidic hydrolysis byproducts (Piemonte et al., 2013). Furthermore, PLA hydrolysis is autocatalytic because hydrolysis creates carboxyl groups that further accelerate the reaction. The rate of hydrolysis is affected by various parameters, including polymer crystallinity, pH, and temperature, as well as the amount of absorbed water, the diffusion coefficient, and the solubility of breakdown products (Schliecker et al., 2005).

Pyrolysis has also been used to assess the recyclability of PHB, with the primary products being crotonic acid and oligomers having crotonate end-groups (Kaihara et al., 2005). Crotonic acid may be polymerized to create copolymers (like vinyl acetate) and poly(crotonic acid), which are used in the creation of dental cements, plasticizers, herbicides, and cosmetic items (Ariffin et al., 2010). The physical shape and purity of the PHB feedstock have a significant impact on the output of crotonic acid. For instance, it was discovered that the yield for pure PHB by dissolving in chloroform was 60–65 percent, but the yield for PHB in dried bacterial cells was 20–25 percent (Norrrahim et al., 2013). In the case of PHBV, the pyrolysis resulted in oligomers of hydroxyvalerate and 2-pentenoic acid.

Furthermore, the final pyrolysis products' relative abundance and rate of degradation might be regulated by adding a catalyst. For instance, CaO and $Mg(OH)_2$ catalysts were used to thermally degrade PHB and PHBV (Ariffin et al., 2010), enabling regulated and selective breakdown at a comparatively low temperature (230°C vs. 290°C). Crotonic acid and 2-pentanoic acid are produced and copolymerized to form poly (crotonic acid-co-acrylic acid), which offers high glass transition temperature, water solubility, prospective uses as hydrogels for the treatment of wastewater and agricultural purposes.

4.5.3. Enzymatic recycling

Enzymatic depolymerization relies on the activity of enzymes and microbes to break down biodegradable bioplastics selectively and controllably in order to recover monomers. This goal is what distinguishes this process as a true recycling method, as opposed to biodegradation and composting, which are instead disposal procedures. Enzymatic and microbiological recycling may be included in the chemical recycling strategies.

The enzymatic depolymerization of biodegradable aliphatic polyesters like PLA, polycaprolactone (PCL), polybutylene succinate (PBS), and poly(butylene adipate) (PBA), using especially lipase or Proteinase-K followed by the depolymerization of the obtained oligomers, has been the subject of numerous research studies and patents, listed in Table 4.2. (Niaounakis, 2019).

Table 4.2. Patents related to the enzymatic and microbial recycling of biodegradable polymers (adapted with permission from (Niaounakis, 2019)).

Biopolymers	**Enzymes/micro-organisms**	**Depolymerization products**	**Patents**
PLA (PLLA, PDLA), PBS	Polypeptide comprising amino acid sequence (SEQ ID No: 1; or SEQ ID No: 5); or micromonospora strain S0002	Lactic acid	WO2016146540 A1 (2016, CARBIOS; CENTRE NAT RECH SCIENT; UNIV POITIERS)
PLA (PLLA, PDLA)	Polypeptide comprising amino acid sequence (SEQ ID No: 1; or SEQ ID No: 5)	Lactic acid, dimers of lactic acid	WO2016062695 A1 (2016, CARBIOS; AGRONOMIQUE INST NAT RECH; INST NAT SCIENCES APPLIQ; CENTRE NAT RECH SCIENT)
PLLA, PTT	Proteinase-K; recombinant strain of Lactococcus lactis or Escherichia coli excreting depolymerase; cutinase	Lactic acid; terephthalic acid	WO2014079844 A1 (2014, CARBIOS)
PLLA, PDLLA, P(LLA-CL) P(LLA-TMC)	Hydrolase; preferably lipase (Novozyme® 435); in organic solvent (xylene, hexane/chloroform) or supercritical fluid (CO_2)	Cyclic ester oligomers	WO2004013217 A1 (2004, UNIV KEIO)

Table 4.2. (continued) Patents related to the enzymatic and microbial recycling of biodegradable polymers (adapted with permission from (Niaounakis, 2019)).

Biopolymers	**Enzymes/micro-organisms**	**Depolymerization products**	**Patents**
PHA (PHB, PHBV), PBS	Hydrolase; preferably lipase (Novozyme® 435); in dichloroethane or acetonitrile	Cyclic ester oligomers	JP2002320499 A (2002, UNIV KEIO)
PCL	Hydrolase; preferably lipase (Novozyme® 435); in toluene	Dicaprolactone	JP2002017385 A (2002, UNIV KEIO)
PCL, PBA, PBS	Hydrolase; preferably lipase; in supercritical fluid (CO_2)	Cyclic caprolactone oligomer, cyclic ester oligomers	JP2003079388 A (2003, UNIV KEIO)
PHB, PCL, PBA, PLA-CL, PTT	Hydrolase; preferably lipase (Novozyme® 435); in supercritical fluid (CO_2) and toluene	Cyclic caprolactone oligomer, cyclic ester oligomers	WO2005026245 A1 (2005, UNIV KEIO)
PBSL	Esterase; preferably cutinase or lipase	Succinic acid	JP2004290130 A (2004, MITSUBISHI CHEM CORP)
PLA, PBS	Proteinase-K (PEOx), lipase CS_2; in ethanol	Monomer and/or oligomer	WO2010050482 A1 (2010, TOYO SEIKAN KAISHA LTD)

4.5.4.Biodegradation, composting, and anaerobic digestion

4.5.4.1.Biodegradation

Biodegradable bioplastics can be degraded through biodegradation, which is also called organic recovery or organic recycling. Biodegradation can occur through anaerobic digestion, biodegradation on agricultural land, or industrial composting. The speed of biodegradation depends on various factors, including the end-of-life pathway, temperature, oxygen and moisture concentrations, and the type and amount of microorganisms. Biodegradation can occur either aerobically (with oxygen) or anaerobically (without oxygen). Composting can be done by fungi, bacteria, and actinomycetes at either moderate or high temperature. Similarly, bacteria perform anaerobic digestion at either high or low temperature. Biodegradation happens more quickly at higher temperatures and in the presence of fungi, which are exclusively present in compost and soil settings. It is important to select the appropriate biodegradation pathway for each type of biodegradable bioplastic, as not all biodegradable plastics break down in all biological degradation conditions (Letcher, 2020).

4.5.4.2.Composting

Composting is an aerobic process resulting in the production of CO_2, H_2O, heat, minerals, biomass, and humus that are beneficial to plant development. Microorganisms including bacteria, yeasts, and fungi are responsible for activating this process. Composting is promoted in the European Union primarily by two directives: the 2008/98/EC Directive on Waste (Directive (EU) 2008/98/EC, 2008), which encourages the separate collection and safe treatment of biodegradable waste, and the EU Council Directive on Landfill of Waste (1999/31/EC) (1999), which calls on member nations to reduce the amount of biodegradable waste that ends up in landfills. It is important to note that while all compostable plastics are biodegradable, not all biodegradable plastics are compostable (Letcher, 2020).

4.5.4.3.Anaerobic digestion

Anaerobic digestion results in three primary products: biogas (high in methane and used as a fuel), biosolids (microorganisms growing on organic matter), and liquor (dissolved organic matter). Anaerobic digestion consists of four major stages: **i)** hydrolysis, which is carried out by bacteria's extracellular enzymes on complex biological macromolecules including carbohydrates, lipids, and proteins to generate simple sugars, fatty acids, and amino acids; **ii)** acidogenesis, which occurs when hydrolysis products are taken by acidogenic microbes, which create intermediates such as volatile fatty acids (VFAs); **iii)** acetogenesis, in which these intermediates are transformed into acetate, hydrogen, and CO_2; **iv)** methanogenesis, in which methanogenic organisms consume intermediates and carbon (Letcher, 2020).

Highlights

- International definitions and economic-environmental relevance of plastics and bioplastics.
- Evaluation of physicochemical properties and source processes of plastics and bioplastics.
- European concepts for distinguishing bioplastics production types and application examples.
- Mechanical recycling of bioplastics is difficult due to thermosensitivity and low crystallization, additives improve recyclability-biodegradability.
- Pyrolysis-solvolysis can convert bioplastics in chemicals and enable a circular economy (they need high temperatures and be energy-intensive).
- Enzymatic and microbiological recycling break down bioplastics to recover monomers-compounds (solution to processes as biodegradation-composting).

Interesting questions

- What are the chemical characteristics of plastics and bioplastics and what are the possible production processes?
- What are the possible chemical and physical properties of bioplastics?
- What are the basic concepts for distinguishing bioplastics and possible matrices for the relative production?
- What are the challenges of mechanical recycling biodegradable plastics, and how can these be addressed?

- In what ways do chemical recycling methods like pyrolysis and solvolysis enable a circular economy for plastic commodities, and what are the potential drawbacks of these approaches?
- How does enzymatic and microbiological recycling differ from traditional methods like biodegradation and composting, and what are the potential benefits and limitations of these approaches for biodegradable plastics?

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CHAPTER 5: CHARACTERIZATION OF BIODEGRADABLE PLASTICS

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5.1.Introduction

Massimo Bersani

The characterization of polymers and plastics involves determining their chemical and physical properties. Chemical properties include the composition of the polymer (which monomers are used and in what ratio), the degree of polymerization (how many monomers are linked together), and any additives that may be included to modify the properties of the material. Physical properties also include mechanical properties (such as strength, stiffness, and elasticity), thermal properties (such as melting and glass transition temperatures), and optical properties (such as transparency and color).

Techniques used to characterize polymers and plastics include spectroscopy, which can be used to identify the chemical structure of the polymer; thermal analysis, which can be used to determine thermal properties such as the melting point and glass transition temperature; and mechanical testing, which can be used to determine the mechanical properties of the material such as strength and elasticity. Other techniques include microscopy, rheology, and chromatography. In general, the characterization of polymers and plastics is an important step in understanding their properties and behavior. This is crucial for designing new materials and improving existing materials.

Polymers are complex materials with a wide range of chemical structures and physical properties, which makes their analysis challenging. Here are some of the main difficulties and problems that can arise in the analysis of polymers:

i) ***Sample preparation:*** The first challenge in polymer analysis is often preparing a representative sample. Polymers can be difficult to dissolve or disperse, and their physical properties can be affected by how they are prepared. For example, mechanical stress during sample preparation can cause changes in the polymer's structure and properties.

ii) ***Variability:*** Polymers can exhibit a high degree of variability due to differences in their molecular weight, degree of branching and other factors. This variability can make it difficult to obtain consistent and reliable results from polymer analysis.

iii) ***Characterization of low-abundance species:*** Polymers can contain low-abundance species such as impurities, degradation products, and additives, which can be difficult to detect and characterize. These species can also have a significant impact on the polymer's properties and behavior.

iv) ***Multi-component analysis:*** Many polymers are blends or composites of different materials, which can make their analysis more complex. Analyzing the different components of a polymer blend can require specialized techniques that are sensitive to differences in chemical structure and physical properties.

v) ***Instrumentation limitations:*** Some techniques used for polymer analysis, such as NMR spectroscopy and mass spectrometry, may require specialized instrumentation and expertise. These techniques can also be time-consuming and may require extensive sample preparation.

vi) ***Data interpretation:*** Finally, interpreting the results of polymer analysis can be challenging, especially when dealing with complex materials that exhibit multiple overlapping signals. Accurate data interpretation requires a thorough understanding of the chemical and physical properties of the polymer as well as the limitations of the analytical techniques used.

In summary, the analysis of polymers can be challenging due to the complexity and variability of these materials, as well as the specialized techniques and expertise required for their analysis (Campbell et al., 2000; Brune et al., 2008). However, overcoming these difficulties is essential for understanding the properties and behavior of polymers and developing new materials with improved performance.

The following sentence can be representative of the difficulties in polymer characterization analyses:

"*We would wish, ideally, to characterize all aspects of a polymer structure in enough detail to predict its performance from first principles. I seriously doubt that this will ever be possible, and I am sure that even if it were, it would never be economically feasible.*" (Billmeyer, 1976).

The goal of the present chapter is to give an overview of polymer characterization. It is structured in five parts: morphological, chemical, mechanical, thermal, functional (optic; electric; dielectric; hydrophilicity...). The first two points are related to micro characteristics, the other three points are related to macro properties. For further information and polymer characterization the publications in the reference list are suggested.

5.2.Morphological Characterization

Massimo Bersani, Laura Pasquardini

The morphological characterization of the biodegradable plastics can be achieved using different microscopy-based techniques obtaining information not only on their surface structure but also on their erosion during the biodegradation process. There are several techniques that can be used for this purpose and are commonly used also for the other types of polymers/plastics. Depending on the scale of the analysis it can be used an optical microscopy reaching a resolution of around 1 µm, or a transmission or scanning electron microscopy going down to the sub-micrometric scale or the atomic force microscopy reaching the nanoscale range resolution (Venkateshaiah et al., 2020). These techniques can be useful to observe the structure of the polymeric chains after the polymerization process, to check for the presence of holes or imperfections and to monitor the effect of degradation by the environment agents.

In the following paragraphs have been reported the main techniques utilized for the morphological characterization of the biodegradable plastics.

5.2.1.Optical and confocal microscopy

Optical microscopy is the simplest among the microscopy techniques. A microscope comprises of two converging lenses, an objective, and an eyepiece utilizes the optical theory of lenses to operate, wherein light emerging from the sample will be collected by the objective and directed towards the eyepiece. Generally, the sample can be illuminated by reflected (episcopic) or transmitted (diascopic) light, giving essential information or insights into the microstructures respectively. The light is generally collected by charge-coupled camera, photodiodes, photomultiplier tubes. The microscope has a theoretical resolution of 200–300 nm in lateral resolution, and 500–700 nm in axial resolution.

When the dimensions of the samples fall into the nanometer scale, variations of optical microscopy have to be used. With the implementation of fluorescence, the diffraction-limited resolution expands to nanoscales and super-resolution is achieved. It can be used confocal, multiphoton, 4Pi microscopy, and structured illumination and spatially patterned excitation to achieve super-resolution in fluorescence spectroscopy.

Laser scanning confocal microscopy (LCSM) is another variant with respect to the conventional wide-field optical microscopy, and it is characterized by the minimization of the background noise from the focal plane, with the possibility to have a 3D reconstruction taking a series of optical sections for thick specimens. An optical filtering technique is used to remove any out-of-focus light from specimens with a thickness exceeding the immediate focus plane. This technique can provide better images than conventional fluorescence microscopy, but LCSM cannot provide nanoscale resolution.

The macroscopic film degradation of biodegradable plastic in situ in compost has been observed and microscopic analysis has been used to determine whether particulates that are added in the production of plastics are released upon degradation (Sintim et al., 2019).

5.2.2.Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM)

The transmission electron microscopy (TEM) works in a similar way of a light microscopy but uses electrons instead of light and being electrons much smaller when compared to that of light, the images obtained from TEM have much higher optical resolution. This enables TEM to reveal the tiniest details of the sample, as small as individual atoms. In a TEM measure, a beam of high-energy electrons passes through very thin samples and can be blocked or deflected from some sample's region and are then collected from below. The dark part of the image represents the areas in the sample through which very few or no electrons are transmitted, respect to the brighter part where more electrons are transmitted, and a range of grey color patterns are obtained depending on the way the electrons interact with the sample. Sample preparation is quite laborious, but it can be obtained information related to topological, morphological, compositional, and crystalline information of biopolymer systems.

The morphology of nanocellulose samples was analyzed via TEM and the aqueous suspension of nanocellulose was found to consist of agglomerating rod-like nanoparticles forming a dense layered structure (Barbash et al., 2016). Lathwal and co-workers instead used TEM analysis to observe the accumulation of dense polyhydroxybutyrate (PHB) granules in the cytosol of bacterial isolates (Lathwal et al., 2018).

Scanning electron microscopy (SEM) uses a high-energy electron beam to scan the samples and provide a high magnification and resolution image. The electron beam interacts with the electrons on the sample and produces signals about the surface topography. The SEM images are obtained by analyzing the signals from the secondary and backscattered electrons. This technique provides information not only about the surface morphology, but also on the sample's crystallinity and the elemental composition when an energy-dispersive X-ray spectroscopy (EDX) is coupled to the instrument. EDX studies on biopolymer systems for instance can help in determining the elemental composition, impurities, chemical modifications, and functionalization of the samples, by providing the elemental composition of the analyzed material and the elemental mapping in the analyzed sample.

The possible resolution is in the order of 1–2 nm, depending on the sample's preparation. The SEM analysis can be carried out under high vacuum or low vacuum and even under wet conditions. Samples for the analysis of SEM are typically coated to avoid surface charging. One variant of conventional SEM is the field emission scanning electron microscopy (FESEM), which provides higher resolution images and a greater energy range, through a highly focused electron beam, which improves spatial resolution and enables the analysis of samples at low potentials. The environmental scanning electron microscopy (ESEM) can instead operate in gaseous atmospheres (air, nitrogen, argon, oxygen, and even water vapor) thus making it possible to carry out "wet imaging" of samples. Using ESEM it is possible to analyze dynamic phenomena such as crystallization, wetting, swelling, drying, melting, freezing, as well as material deformation.

SEM imaging is widely used to determine the surface topography, homogeneity, and any phase separation between different components in a biopolymer and composite film.

It has been used for instance for the examination of the surface of different plastics after 32 weeks in the salt marsh, observing a moderate degradation characterized by pitting, microcracks, and occasional areas where it appeared that the overlying surface layers had been removed (Weinstein et al., 2020).

The compatibility between wood and poly(butylene adipate-co-terephthalate) PBAT has been checked via SEM analysis, displaying good filler matrix interaction for esterified wood, whereas composites showed poor interface between the phases without esterification (Yu et al., 2022). The biodegradation of poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) fibers has been assessed via SEM analysis highlighting differences in the microstructure of untreated and treated composites (Hammiche et al., 2020).

5.2.3.Atomic force microscopy (AFM)

Atomic force microscopy has become a preferred technique for characterizing polymers in general. The main advantages are that it is not necessary to work in a vacuum environment during analysis or to cover the samples with a conductive layer; moreover, it is possible to directly measure height and roughness with atomic resolution. In addition, the AFM technique does not require prior complex sample treatment for the characterization of the morphology, microstructure, and crystallinity of different polymer films.

The interaction between tip and surface, while they are in contact or are extremely close, is governed by different types of forces. The main ones are the Van der Waals interaction, the Coulomb force, and the capillary effect. At extremely small distances, Van der Waals interactions, usually masked by the electrostatic force, become important.

The AFM can work in different ways depending on the type of interaction between the tip and sample and the surface characteristics to be analyzed. The two commonly used methods are in contact mode and in non-contact mode. In contact mode, the tip is in contact with the surface of the sample, and the interaction is regulated by the Van der Waals interaction between the tip and sample. The surface of the sample is approached to the tip until the interaction between the two becomes repulsive. At this point, the cantilever is deflected and kept constant by the electronics of the scanner electronics throughout the scan. The sample is moved in x and y directions, such that the tip describes a straight line in either direction, e.g. along x and y. When the tip encounters an obstacle or depression on the surface, the cantilever begins to bend and the diode detects a change in light intensity.

In the non-contact mode instead, the cantilever is brought close to the sample and begins to interact with it, lightly striking the surface with each oscillation. In this way, the tip is in contact with the sample for less time, so it is less likely to cause drag, breaking both the sample and itself. The selection of the working mode depends on the sample characteristics. An image of the instrument principle is reported in Figure 5.1.

The spatial resolution of an AFM instrument can be divided into two parts: the resolution in the z-axis perpendicular to the sample surface and the lateral resolution in the x and y directions. The vertical resolution Δz is defined as the minimum height difference which can be detected by the instrument, that strongly depends on the elastic properties of the sample and the parameters of the instrument, and the measurement (scanning speed, size of the examined area, parameters of the feedback system). Dealing with an ideal sample and ideal parameters, the vertical resolution can be up to a few tenths of ˚A. Since the AFM tip is not infinitely thin but has its own dimension, the lateral resolution depends on the radius of curvature. To give an example, if we assume a vertical resolution of 1˚A the typical lateral resolution for a tip with a radius of curvature of 10 nm is about 3 nm.

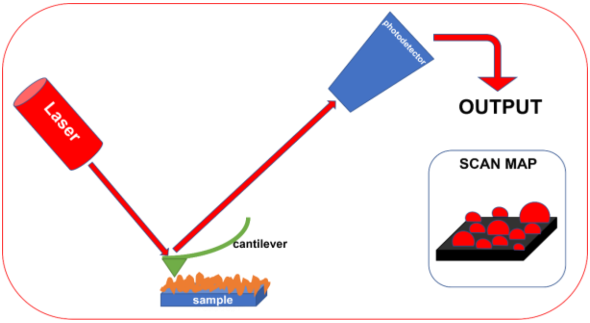


Figure 5.1. Scheme of the AFM imaging and relative output

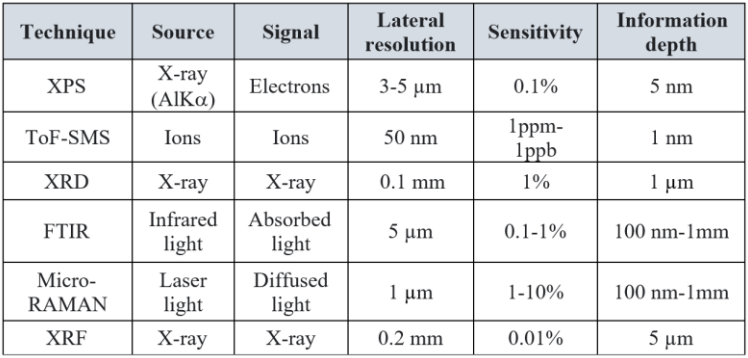
AFM imaging has been used by Wu and co-workers to check the morphology of PLA/PBS/PBAT ternary blends before and after the extrusion with peroxide (Wu et al., 2020). The AFM images suggested that depending on the ratio of these three polymers, the PBAT-PBS core-shell phase in the blends was transformed into a droplet phase or in a co-continuous phase. The surface topography and three-dimensional structure of starch-based bioplastic has been studied through AFM, showing a rough surface with ungelatinized starch granules compared to the crosslinked films where the film was not cross-linked (Chakraborty et al., 2022). Coaxial electrospun fibrous scaffold with a core of polylactic acid (PLA) and a shell of polyvinylpyrrolidone (PVP) loaded with an antibiotic for the prevention of infections until the wound healing have been produced and AFM analysis have been used to characterize the electrospun fibers (Hajikhani et al., 2021); the fiber surface roughness directly affects the fiber adhesion to the tissue surface.

5.3.Chemical Characterization

Massimo Bersani, Laura Pasquardini

The chemical characterization of the biodegradable plastics can be achieved using different techniques. The main information can be achieved through X-ray photoelectron spectroscopy (XPS), Time of flight secondary ion mass spectrometry (ToF-SIMS), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), micro-RAMAN spectroscopy and X-ray fluorescence (XRF). In the following paragraphs, these techniques will be briefly illustrated, and the main applications related to the characterization of biodegradable plastics will be reported. In Table 5.1, the main parameters related to the techniques described in the chapter, are listed, and compared.

Table 5.1. Summary of the main parameters related to the chemical analysis techniques.



Technique	Source	Signal	Lateral resolution	Sensitivity	Information depth
XPS	X-ray (AlKα)	Electrons	3-5 μm	0.1%	5 nm
ToF-SMS	Ions	Ions	50 nm	1ppm-1ppb	1 nm
XRD	X-ray	X-ray	0.1 mm	1%	1 μm
FTIR	Infrared light	Absorbed light	5 μm	0.1-1%	100 nm-1mm
Micro-RAMAN	Laser light	Diffused light	1 μm	1-10%	100 nm-1mm
XRF	X-ray	X-ray	0.2 mm	0.01%	5 μm

5.3.1.X-rays photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) or Electron spectroscopy for chemical analysis (ESCA) is a technique useful to identify the elements present on the polymeric surface.

The theoretical basis of the technique is founded in modern physics, following Heinrich Hertz’s discovery of the photoelectric effect in 1887. In the 20th century, Albert Einstein investigated this effect and laid the foundations of the quantum theory. The phenomenon concerns what happens when the matter is bombarded with electromagnetic radiation: electrons are emitted from the orbitals of the atoms of the surface, by a process called photoionization. By measuring the energy with which these electrons are emitted, it is possible to have information on both the nature of the atom from which they originate and its chemical surroundings. The formula that describes the energy balance of the photoemission and which forms the basic relation of XPS is the following:

$KE = h\nu - BE - \Phi$

where KE is the kinetic energy of the emitted photoelectron as measured by the detector, $h\nu$ is the energy of the photon beam used to excite the sample, BE is the binding energy of the electrons and Φ is the work function of the instrument (parameter calculated independently for each instrument and used as a constant) (Briggs, 1998).

The technique generally provides information on elements present within a few nanometers of the sample surface (5-10 nm) with a lateral resolution of about 10 μm. The principle of XPS is illustrated in Figure 5.2.

When insulating material samples, such as plastics, are analyzed, a positive charge occurs during the X-ray irradiation inside the analyzed area due to the generation of photoelectrons and a charge neutralization is necessary during measurement to maintain a good signal and a high energy resolution. Through this technique is also possible to carry out a depth profile, using an ion sputtering gun to perform the surface etching. The first outputs of the measure are the survey spectra, where it is possible to identify the elements (looking at different peaks with different binding energy). Analyzing the core lines with a higher energy resolution it is possible to discriminate the different chemical bonds. The imaging allows to correlate the element with its position on the analyzed sample area.

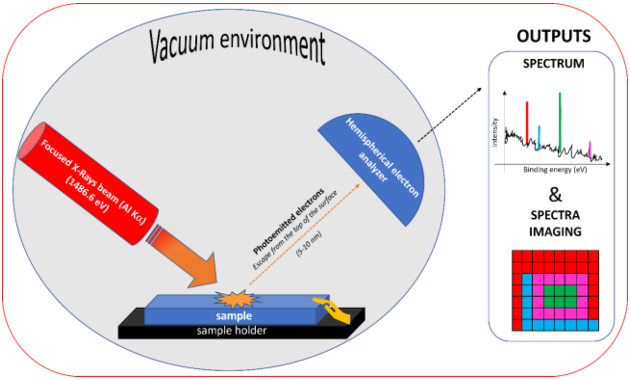


Figure 5.2. Scheme of the XPS analysis and of outputs of the measurement

Recently, XPS analysis has been used to determine the effect on the chemical structure of biodegradable plastics (hybrids of polylactic acid (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) with additives) caused by the light irradiation. Results suggested that during the light irradiation process, the C-C/C-H (including aromatic carbon) species interacted with free radicals (due to the presence of air and humidity), changing into C-O/C=O/O-C=O groups (Chang et al., 2022). Another example is reported by Ghasemlou et al., where the soil biodegradation of (polyhydroxy urethanes) PHUs and hybrids made of PHUs within starch bioplastics has been studied (Ghasemlou et al., 2022). The decrease in the O/C ratio can be used to explain the changes in the components during the biodegradation process. Sourkouni and coworkers instead, used XPS analysis to evaluate the changes in oxidation produced by ultrasonication, UV photodegradation and their combination as well as dielectric barrier discharge plasma as pre-treatment technologies for helping bacteria in the biodegradation mechanism (Sourkouni et al., 2021). XPS analysis is therefore useful for monitoring the chemical changes occurring due treatments or degradation processes.

XPS has become very useful for surface polymers analysis. The capability of XPS to define different functional groups is a strong advantage. The study of carbon peaks allows to obtain several information on bonds in the molecules. Typical applications are the evaluation of content and distribution of additive elements in polymers (Briggs and Seah, 1983) and studies of incorporated micro and nano fibers. Examples of applications of XPS on polymers can also be found in early studies (Siegbahn et al., 1967).

5.3.2. Secondary ion mass spectrometry (SIMS) and Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

Secondary ion mass spectrometry (SIMS) is an ultra-surface sensitive, ultra-high vacuum analytical technique capable of probing the top 1-2 nanometers of a sample’s surface. An ion (the primary ion) is accelerated towards the surface of interest, with energy generally between 0.5 and 20 KeV and, because of the impact of the ion with that surface, a large number of particles are ejected into the vacuum (e.g., neutral atoms, ions, electrons, and molecules). This phenomenon is called erosion or sputtering. A small portion of these particles are ions (positive and negative secondary ions), which are collected and separated in a mass spectrometer (analyzer).

The secondary ions are representative of the species that make up the surface, and so SIMS is a technique that can acquire chemical information from a surface.

In 1910 Joseph J. Thomson first observed the particles emitted by a sample by bombarding it with a beam of primary ions, being able to correctly interpret the positive secondary ions produced by the bombardment of a metal sample inside a discharge tube. The construction of the first experimental apparatus was in 1949 by Herzog and Viehbock.

In this case, the spectrometer is a Time-of-Flight spectrometer (ToF-SIMS), and the primary ion beam is pulsed (Belu et al., 2003). The secondary ions emitted by the sample are separated according to their mass by the time-of-flight detector, and the spatial information of where the spectrum was acquired is maintained; so that the extracted ions can be displayed in the form of a spatial map (Figure 5.3). For imaging, spatial resolution below 100 nm is attainable with current liquid metal ion guns (LMIGs) (Gunnarsson et al., 2010). Secondary ion yields have been greatly enhanced through the adoption of polyatomic ion sources (Weibel et al., 2003).

When measuring insulating materials, a pulsed low-energy electron flood is employed to prevent charge build-up on the sample due to primary ion irradiation. Using ToF-SIMS it’s possible to obtain information regarding elements or molecular species at a very high detection sensitivity.

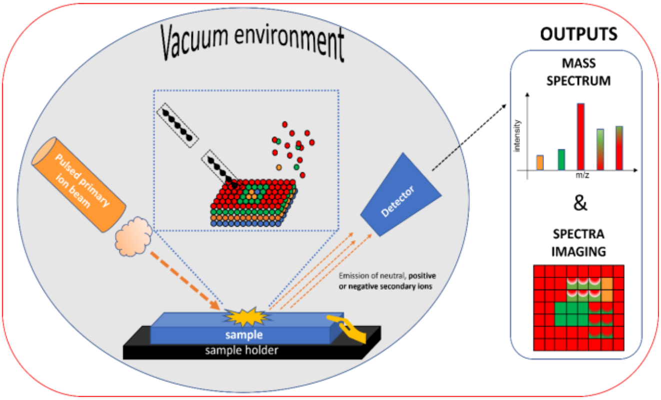


Figure 5.3. Scheme of the ToF-SIMS analysis and of measure's outputs.

Using TOF-SIMS two main processes can be observed in the spectra of polymers, the fragmentation of polymer chains and the desorption of intact oligomers. It has been used for instance to access the hydrolytic degradation of poly(α-hydroxy acid)s [e.g., poly(glycolic acid) (PGA), poly(L-lactic acid) (PLLA), and poly(lactic-co-glycolic acid) (PLGA)] as a function of hydrolysis time in various pH buffer media (Lee and Gardella, 2002) or in wood-polymer composites where analysis with high spatial and depth resolution have been obtained (Stroka and Goacher, 2016). The ToF-SIMS analysis offers the ability to monitor different changes inside a sample. For instance, variations in chemical proportions over time through spectral analysis or the chemical species distribution on the sample surface over time through image analysis, allowing for a greater chemical understanding of the surface and also, through depth profile analysis, just below the surface. Other applications are the analysis of polymer surface modification by plasma treatment (Strobe et al., 1994); surface segregation in polymer blends (Lhoest et al., 1995); and analysis of carbon fibers used for polymer functionalization (Weng et al., 1995).

5.3.3.X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique useful for characterizing crystalline materials both bulk materials and thin films. With this technique, it’s possible to have information on crystal structure, phase, referred crystal orientation (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects without a vacuum environment for the analysis.

A monochromatic beam of X-rays diffracts at specific angles and the diffraction pattern is the fingerprint of the periodic atomic arrangements in each material.

XRD technique generally provides information between ≈20 Å up to ≈30 μm, depending on the material properties and the X-ray incidence angle, with a lateral resolution in the mm range (apart from microdiffraction has a lateral resolution of about 20 μm. A scheme of the technique is reported in Figure 5.4.

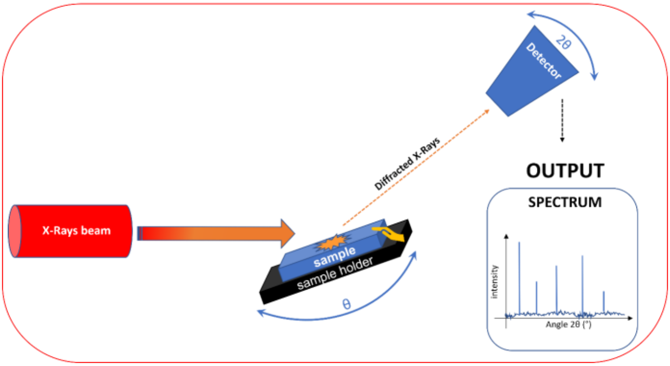


Figure 5.4. Scheme of the XRD analysis and of measure's outputs.

XRD has been used to check the chemical changes after degradation in polypropylene composites prepared using natural fibers (such as pigeon, pea stalk fibers and banana peel) (Luthra et al., 2020); the increase in the crystallinity after degradation suggested that the amorphous part of the composite degrades first. Xia and co-workers used XRD to assess the changes in crystallinity of a lignocellulosic bioplastic synthesized by in situ lignin regeneration, observing that the patterns of the wood powder, cellulose and lignocellulosic bioplastic exhibited similar diffraction peaks, confirming the preservation after the in-situ lignin regeneration treatment (Xia et al., 2021).

5.3.4.Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is one of the most used techniques for chemical characterization and is based on the adsorption of infrared light by the sample, which causes a change in the vibrational energy in the chemical bond. Since different bonds and functional groups absorb different frequencies, the transmittance pattern is different for different molecules. It is a non-destructive technique, quick, sensitive, and precise.

The first instrument was produced by Perkin-Elmer in 1957. A scheme of the method is reported in Figure 5.5.

FTIR is limited to a spatial resolution of ~5 µm and a depth information of less than 1 µm.

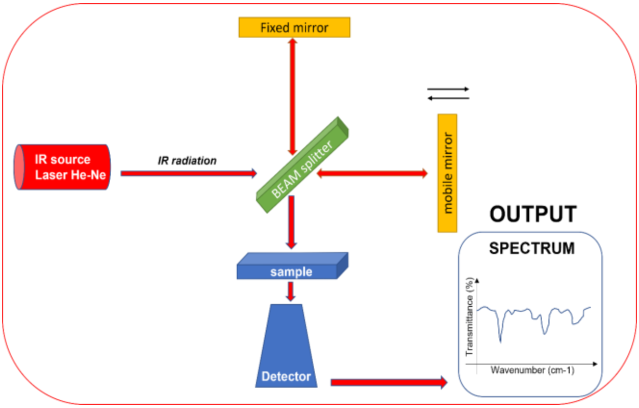


Figure 5.5. Scheme of the FTIR analysis and the measurement's output.

The biodegradable and oxo-biodegradable shopping and waste bags have been analyzed using FTIR analysis to monitor the structure and degree of decomposition in an industrial composting implant (Markowicz and Szymańska-Pulikowska, 2021). Sandt and co-workers instead used this technique to study the levels of plastic oxidation as evidence of degradation. The creation of new C-O, C=O, and O-H bonds during oxidation is clearly attributed to the degradation with respect to the spectral signatures of biomass contamination (Sandt et al., 2021). FTIR has been also used to identify the effects of molecular interactions involved between gelatin, carboxymethyl cellulose, and agar on a film’s structure, to confirm the correlation of functional group and structure of composite blended bioplastics (Yaradoddi et al., 2020).

5.3.5.Micro-RAMAN

The micro-RAMAN technique is a spectroscopic technique typically used to determine vibrational modes of molecules that are closely related to the chemical bonds inside the material. Raman spectroscopy provides information on intra- and intermolecular vibrations and can provide a characteristic spectrum of the specific vibrations of a molecule (a kind of “molecular fingerprint”) useful for identifying a substance, allowing a better understanding of the structure of the molecular backbone and crystal lattice. The instrument uses a source of monochromatic light (usually a laser in the visible, near infrared, or near ultraviolet range) that interacts with molecules generating scattering effects. A small amount of radiation is scattered at a wavelength different respect to the incident light. The Raman effect which in 1930 brought the Nobel Prize to the Indian physicist, Sir Chandrasekhara Venkata Raman. It is a non-destructive method and one of the most used spectroscopic techniques for plastic characterization (Adarsh et al., 2022). Figure 5.6 reports the scheme of the technique and the expected output.

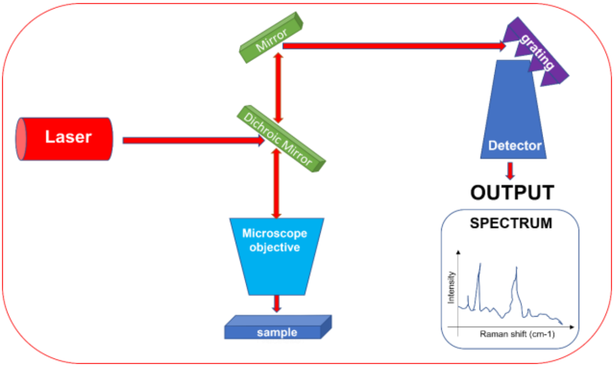


Figure 5.6. Scheme of the micro-RAMAN analysis and, the measurement's output

In a recent literature work, it has been highlighted that Raman spectroscopy can analyze microplastic particles in a range of 1 and 20 µm in diameter and 1 pg to 1 µg in mass (Anger et al., 2018). The fingerprint region of different kinds of plastic have been reported, suggesting the high ability of this technique in the recognition of specific material. Analysis on poly (lactic acid), poly (butylenes adipateco-terephthalate), poly (hydroxybutyrate-co-hydroxyvalerate) and poly (butylenes succinate) have been reported by Cai and co-workers (Cai et al., 2013) finding fingerprint bands useful in the identification of the four biodegradable plastics.

5.3.6.X-ray fluorescence spectroscopy (XRF)

X-ray fluorescence spectroscopy (XRF) is a non-destructive analytical technique that can be used to determine the elemental composition of a material. XRF works by irradiating a sample with high-energy X-rays, which causes the characteristic emission from the atoms in the sample of a X-ray fluorescence radiation. The configuration of the instrument is similar to Figure 5.4, with the difference that a fixed position of the sample is used. The intensity of the fluorescence radiation is then measured and used to determine the elemental composition of the sample.

In polymer analysis, XRF can be used to determine the elemental composition of a polymer sample, which can provide valuable information about the material’s properties and potential applications. For example, XRF can be used to determine the levels of additives, such as fillers or pigments, in a polymer sample. It can also be used to identify contaminants, such as metals or other foreign substances, which can impact the material’s performance. XRF can be particularly useful in analyzing polymer composites (Janssens et al., 2010), which are made up of multiple components, such as a polymer matrix and reinforcing materials like fibers or particles. XRF can be used to determine the elemental composition of each component, which can help to understand the material’s structure and properties.

XRF is a non-destructive technique, indeed the sample is not damaged during the analysis. This makes XRF a valuable tool for polymer analysis, as it allows for multiple analyses to be performed on the same sample without the risk of damaging or altering the material.

5.4.Mechanical characterization of biodegradable plastics

Giulia Fredi, Alessandro Pegoretti

5.4.1.Introduction

Biodegradable polymers and plastics have gained increasing attention in recent years and their use has expanded to various fields such as packaging, agriculture, medical, and textile applications. However, it is essential to fully characterize the mechanical properties of these materials to ensure their performance and suitability for such applications. In this chapter, we will discuss the mechanical characterization of biodegradable polymers and plastics, including the methods of characterization, the associated international standards, and the molecular and microstructural factors affecting the mechanical properties.

5.4.2.Methods of mechanical characterization

Mechanical characterization is the process of measuring the mechanical performance of a material under different loading conditions. Mechanical characterization techniques for biodegradable plastics can be divided into short-term testing and long-term testing. Short-term testing techniques include tensile, compressive, flexural, impact, hardness, fracture toughness, shear, and tear testing, while long-term testing includes creep, stress relaxation, and fatigue testing, as well as environmental stress cracking (ESC), accelerated aging, and weathering testing. Some of these techniques are described in the rest of this chapter.

5.4.2.1.Tensile testing

Tensile testing is a commonly used method for evaluating the mechanical properties of materials, including biodegradable polymers and plastics. This technique measures the resistance of a material to a stretching or pulling force, which is applied at a well-defined and generally low (1-100 mm/min, quasi-static characterization) rate until the sample fractures. The most important international standards for tensile testing of polymers and plastics are ISO 527 and ASTM D638.

The test is typically conducted using a universal testing machine, which applies a tensile load to a specimen with a well-defined geometry (e.g., dumbbell specimens) of the material at a defined and constant rate. During the test, the machine measures the force applied and the corresponding deformation of the specimen until it breaks. The results of the test provide valuable information about the mechanical behavior of the material under tension.

The most important properties derived from the tensile test include the elastic modulus, tensile strength and strain at yield, and tensile strength and strain at break. For example, the elastic modulus, or Young’s modulus, is a measure of the material’s stiffness and is determined by the slope of the initial linear region of the stress-strain curve. The tensile strength is generally regarded as the maximum stress that the material can withstand before it breaks, while the stress and strain at break are the last stress and strain values at the point of failure.

These properties are essential for evaluating the suitability of biodegradable polymers and plastics for various industrial applications. For example, a high elastic modulus indicates that the material is stiff and has good dimensional stability, a high tensile strength is critical for applications where the material needs to withstand high stress, while a high strain at yield and break generally indicates a high toughness and the capability of the material to sustain a large deformation before rupture. Hence, tensile testing is a key method for characterizing the mechanical properties of biodegradable polymers and plastics, providing essential information for evaluating their performance and suitability for various industrial applications (Van Krevelen and Nijenhuis, 2009).

5.4.2.2.Compressive testing

Another commonly used mechanical characterization technique is compressive testing, which also falls among the quasi-static characterization methods and measures the resistance of a material to a compressive force applied gradually until the sample fractures. The most important international standards for compressive testing of polymers and plastics are ISO 604 and ASTM D695.

The test is typically conducted using a universal testing machine, which applies a compressive load to a cylindrical or cuboid-shaped specimen of the material at a constant rate. During the test, the machine measures the force applied and the corresponding deformation of the specimen until it breaks. The most important properties derived from the compressive test include the compressive strength and modulus, which are analogous to the tensile strength and modulus, respectively. Compressive strength is the maximum stress that the material can withstand before it breaks under compression, while the compressive modulus is a measure of the material’s stiffness under compression.

These properties are essential for evaluating the suitability of biodegradable polymers and plastics for various industrial applications that involve compression forces. For example, compressive strength is critical for applications where the material needs to withstand heavy loads, such as in construction or industrial packaging.

5.4.2.3.Flexural testing

Flexural testing, also known as bend testing, is another widely used method for evaluating the mechanical properties of biodegradable polymers and plastics. This technique measures the resistance of a material to bending forces applied to a slender, rectangular-shaped specimen. The most important international standards for flexural testing of polymers and plastics are ISO 178 and ASTM D790.

The test is typically conducted using a universal testing machine equipped with a three-point or four-point bending fixture. In three-point bending, the sample is supported at two points and a load is applied at the midpoint of the sample, while in four-point bending, the sample is supported at two points, and a load is applied at two points equidistant from the supports. During the test, the machine measures the force applied and the corresponding deflection of the specimen until it breaks. The results of the test provide valuable information about the mechanical behavior of the material under bending or flexural loads.

The most important properties derived from the flexural test include the flexural modulus, flexural strength, and strain at break. The flexural modulus is a measure of the material’s stiffness under bending, while the flexural strength is the maximum stress that the material can withstand before it breaks under bending. The flexural strain at break is also determined in a similar way as the tensile and compressive strain.

5.4.2.4.Impact testing

Impact testing is an important tool for evaluating the toughness and resistance of biodegradable polymers and plastics to fracture under dynamic loading conditions. Several international standards are available for conducting impact tests on these materials, including ASTM D256 (for Izod impact strength), ASTM D4812 (for falling dart impact), and ISO 6603 (for Charpy impact strength). The schematic representation of the Charpy and Izod impact testing is reported in Figure 5.7.

In the Izod impact test, a notched specimen is clamped vertically and then struck horizontally with a pendulum at a known speed and releasing a known energy. The energy required to break the specimen is measured and reported as the Izod impact strength. Charpy impact strength is determined by striking a horizontally-lying notched specimen with a pendulum, and the amount of energy absorbed by the specimen during fracture is measured. Falling dart impact testing involves dropping a dart of known mass from a known height onto a specimen held in a fixture, and the impact energy required to cause a specified level of damage is determined.

The most important properties derived from impact testing include impact strength, ductile-to-brittle transition temperature, and the energy absorbed during fracture. These properties are crucial for industrial applications of biodegradable polymers and plastics, as they can provide valuable information regarding the durability and toughness of the material under different loading conditions. The impact resistance of a material is particularly important for applications where the material is likely to experience sudden or unexpected impacts.

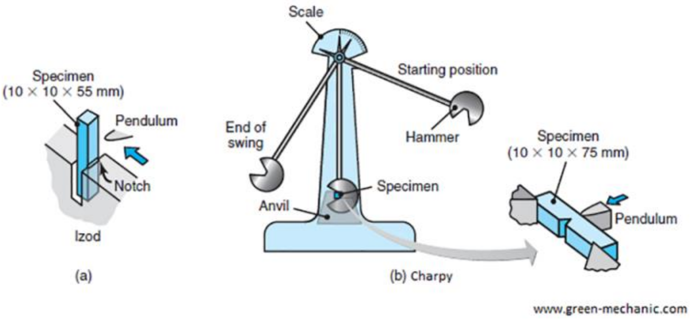


Figure 5.7. Schematic representation of impact testing characterization. Charpy and Izod configurations (duplicated from (https://www.centexbel.be/en/testing/charpy-izod-impact-tests))

5.4.2.5.Hardness testing

Hardness is an important mechanical property of biodegradable polymers and plastics, as it relates to the material’s ability to resist permanent indentation or scratching. Several international standards are available for conducting hardness tests on these materials, including ASTM D2240 (for Shore hardness), ISO 868 (for durometer hardness), and ASTM D785 (for Rockwell hardness). For example, in the Shore hardness test, a durometer is used to measure the resistance of the material to indentation by a spring-loaded indentor. The Shore hardness value is reported as a number between 0 and 100, with higher values indicating greater hardness.

This test gives information about the material’s hardness, which is correlated to other technological properties such as the resistance to scratch and wear. These properties are crucial for industrial applications of biodegradable plastics, especially where the material will be exposed to abrasive or scratching conditions.

5.4.2.6.Fatigue testing

Fatigue testing is used to evaluate the long-term performance of materials under cyclic loading conditions and is particularly important for applications where components experience repeated loading and unloading. These tests are performed according to several international standards, including ISO 1099 and ASTM D3479.

In a typical fatigue test, the specimen is subjected to cyclic loading at a specified frequency and amplitude. The loading conditions can be either constant amplitude or variable amplitude, which simulates real-life conditions more accurately but is less translatable into material-specific parameters. The number of cycles required to cause failure is recorded and the results are used to plot the S-N curve, which shows the relationship between the applied stress amplitude (S) and the number of cycles to failure (N).

The most important properties derived from the fatigue test are the fatigue limit, also known as the endurance limit, and the fatigue life. The fatigue limit is the maximum stress level that the material can withstand for an infinite number of cycles without failing. The fatigue life is the number of cycles that a material can withstand at a given stress level before failing.

5.4.3. Factors affecting the mechanical properties of biodegradable plastics

The mechanical properties of biodegradable polymers can be affected by several factors such as their chemical structure, molecular weight, degree of crystallinity, processing conditions, and environmental factors.

The chemical structure of biodegradable polymers and their crystallinity plays a significant role in determining their mechanical properties. For example, polylactic acid (PLA) is a biodegradable polymer that can be produced from either L-lactide or D,L-lactide monomers. PLA produced from 100 % L-lactide monomers is more crystalline and hence exhibits higher stiffness and tensile strength than PLA produced from D,L-lactide monomers, but generally a lower strain at break. Another example is given by the polyhydroxyalkanoates (PHA), biodegradable polymers that can be produced from various monomers, such as 3-hydroxybutyrate (3HB), 3-hydroxyvalerate (3HV), and 4-hydroxybutyrate (4HB). Their mechanical properties can be tailored by producing copolymers with a specific comonomer ratio and order.

The molecular weight affects the polymer’s behavior in terms of viscosity, strength, and toughness. In general, a higher molecular weight leads to higher strength and toughness of a polymer, while a lower molecular weight results in lower viscosity. A higher molecular weight determines an increased number of entanglements, which makes the polymer more resistant to deformation and increases its strength and toughness. Furthermore, the molecular weight distribution of a polymer also affects its mechanical properties. A narrow molecular weight distribution can result in a more consistent and predictable behavior of the polymer, while a broad distribution can lead to more variable properties (Ward and Sweeney, 2004).

Processing conditions, such as temperature, pressure, and extrusion rate, can also affect the mechanical properties of biodegradable polymers. For example, increasing the extrusion rate during processing can lead to an increase in the tensile strength of PLA due to molecular orientation and crystallinity. Finally, environmental factors such as temperature, humidity, and UV exposure can also affect the mechanical properties of biodegradable polymers. For instance, the mechanical properties of polycaprolactone (PCL) can be significantly affected by exposure to water, which can lead to a decrease in its tensile strength.

5.4.4.Conclusions

In conclusion, the mechanical properties of biodegradable polymers and plastics play a crucial role in determining their suitability for various industrial applications, which claims for a proper application of mechanical characterization techniques. Tensile, compressive, flexural, impact, hardness, and fatigue tests are widely used to evaluate these properties, with various international standards available for each testing method. The resulting mechanical properties can be affected by their chemical structure, molecular weight, degree of crystallinity, processing conditions, and environmental factors, but also by the testing conditions such as the testing speed. Understanding these factors and the output of the mechanical characterization techniques is essential for the development of biodegradable polymers with tailored mechanical properties that meet the requirements of specific applications.

5.5.Thermal characterization of biodegradable plastics

Giulia Fredi, Alessandro Pegoretti

Thermal analysis is a group of techniques that measure a material’s response to changes in temperature. These techniques are used to establish a relationship between temperature and specific physical properties of materials. Common techniques include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis, dynamic mechanical thermal analysis (DMTA), dielectric analysis, and micro/nano-thermal analysis. Thermal analysis is used in the plastics and bioplastics industry and other industries that use polymers to measure physical properties, understand thermal and mechanical histories, design processes, and estimate lifetimes in various environments. As a result, thermal analysis is a crucial research and quality control method in the development and production of polymeric materials and industries that use these materials in their products. The most important thermal analysis techniques applied to biodegradable polymers are listed in Table 5.2. The three upcoming subchapters will deal with three of the most important and widely used thermal analysis techniques for plastics in general and biodegradable plastics in particular, i.e., DSC, TGA, and DMTA.

Table 5.2. Main thermal characterization techniques for biodegradable polymeric materials (adapted from (Menczel and Prime, 2009)).

Method	Acronym	Property measured
Differential Scanning Calorimetry	DSC	Glass transition temperature, melting and crystallization temperature and enthalpy, degree of curing, curing enthalpy, specific heat capacity
Thermogravimetric Analysis	TGA	Thermal degradation temperature, composition
Thermomechanical Analysis, Thermodilatometry	TMA	Thermal expansion coefficient
Dynamic Mechanical Thermal Analysis	DMTA	Viscoelastic parameters (storage modulus, loss modulus, loss factor)
Dielectric Analysis	DEA	Dielectric properties
Light Flash Analysis	LFA	Thermal diffusivity, specific heat capacity

5.5.1.Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique that evaluates the temperature-dependent heat flow rate differential between a substance and a reference. This technique is used to calculate numerous temperature characteristics, such as heat capacity, melting and crystallization temperatures, and heat of fusion, as well as thermal parameters of chemical reactions. DSC is widely employed in the polymer and pharmaceutical industries, as well as inorganic and organic chemistry, and is regarded as the “workhorse” of thermal analysis. Gray and O’Neil of the Perkin-Elmer Corporation pioneered the technique in 1963, and it has since increased in popularity, with an estimated 100,000 publications on the subject per year.

The main advantages of DSC include its ability to determine the glass transition temperature, heat capacity jump at the glass transition, melting and crystallization temperatures, and heat of fusion, as well as its ability to quickly determine the purity of a sample and evaluate the kinetics of chemical reactions such as thermal and thermo-oxidative degradation. In recent years, innovative approaches in DSC have been introduced, including pressure DSC, fast-scan DSC, and modulated temperature DSC. DSC is particularly advantageous when only a small amount of sample is available, as it only requires milligram quantities for measurements.

There are two types of DSC instruments: heat flux and power compensation. Heat flux DSC emerged from differential thermal analysis (DTA) and typically consists of a device with a reference and sample holder separated by a bridge that works as a heat transfer mechanism, encased in a constant temperature block. The heater, sensors, and holder platforms are all located in this block. The heat transfer bridge allows for the rapid movement of heat in order to achieve a steady state. The difference in behavior between the sample and the reference is used to assess the sample’s thermal characteristics. A temperature sensor is situated at the base of each platform. In power compensation DSC, the sample and reference holders are heated at a constant rate by an average amplifier. The sample holder will have a temperature lag during heating because it has a higher heat capacity than the reference holder. A differential amplifier is used to supply additional heat to balance the temperature of the sample holder with that of the reference holder. In the absence of chemical processes or thermal transitions, the DSC trace records the power from the differential amplifier as a function of the temperature program, and this power is roughly proportional to the heat capacity of the sample.

5.5.2.Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a method of measuring the mass of a polymer as it is exposed to a controlled temperature program in a controlled atmosphere. The temperature range for commercial TGA equipment is typically from room temperature to 1000°C or higher, making it suitable for analyzing polymers. The atmosphere in which the sample is analyzed can be inert (nitrogen, argon, or helium), oxidizing (air or oxygen), or reducing (forming gas, i.e., 8-10% hydrogen in nitrogen), even though with polymers a reducing atmosphere is rarely needed.

Polymers typically exhibit mass loss during TGA, although mass gain can be observed under certain conditions. The mass loss can be categorized as being due to volatile components (up to 300°C), reaction products (e.g., water and formaldehyde from the cure of phenolic and amino resins, generally between 100°C and 250°C), or degradation products resulting from chain scission (200-800°C). The measurement of these mass losses can provide information on the composition, extent of cure, and thermal stability, and the kinetics of such processes can be also determined for the modeling and prediction of cure, thermal stability, and aging.

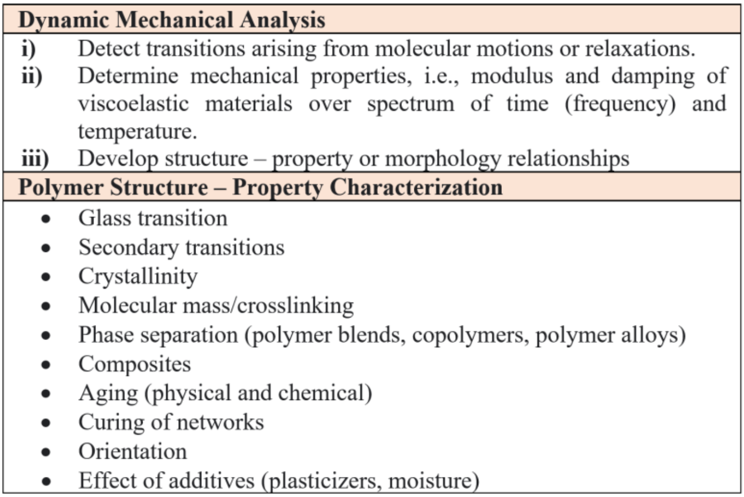
5.5.3.Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) is a widely used technique to characterize the thermal, mechanical, and rheological properties of polymers, including biopolymers and bioplastics. The technique measures the mechanical and viscoelastic properties of polymers as a function of temperature and time by applying small sinusoidal stress and monitoring the resulting strain (or vice versa). This information provides insight into the polymer’s molecular structure and behavior, including its elasticity, viscoelasticity, glass transition temperature, and other secondary relaxations.

The use of DMTA in characterizing bioplastics is particularly important for determining their suitability for various applications, such as packaging, medical devices, and automotive components, among others. DMTA has been also used to evaluate the effects of processing conditions, such as temperature, humidity, and shear rate, on the physical properties of biopolymers and bioplastics. These results can be used to optimize processing conditions and improve the performance of these materials in various applications, such as packaging and biomedical materials. Overall, DMTA is a valuable tool for understanding the complex behavior of biopolymers and bioplastics and for developing new materials with improved properties.

Table 5.3 highlights the main applications of DMTA and structure-property characterization.

Table 5.3. Main applications of DMA and Structure - Property Characterization (adapted from (Menczel and Prime, 2009)).



Dynamic Mechanical Analysis	
i)	Detect transitions arising from molecular motions or relaxations.
ii)	Determine mechanical properties, i.e., modulus and damping of viscoelastic materials over spectrum of time (frequency) and temperature.
iii)	Develop structure – property or morphology relationships
Polymer Structure – Property Characterization	
•	Glass transition
•	Secondary transitions
•	Crystallinity
•	Molecular mass/crosslinking
•	Phase separation (polymer blends, copolymers, polymer alloys)
•	Composites
•	Aging (physical and chemical)
•	Curing of networks
•	Orientation
•	Effect of additives (plasticizers, moisture)

The goal of a typical DMTA test is to determine the mechanical properties such as storage modulus, loss modulus, and damping factor of a material. A typical DMTA test involves the following steps:

i) ***Sample preparation:*** The sample is typically prepared by cutting a small piece of material, with a known and constant cross-section, that is mounted between the clamps of the DMTA testing device. The sample is usually conditioned to a specified temperature and humidity prior to testing.

ii) ***Specimen loading:*** The sample is then subjected to a dynamic load, usually by applying a sinusoidal strain or stress. The frequency of the load can be swept from low to high frequencies, while the temperature is maintained constant or ramped up or down.

iii) ***Data collection:*** The test instrument measures the resulting dynamic mechanical response of the sample, including changes in strain or stress, and the phase shift between the applied and resulting mechanical signals. The data is then analyzed to determine the mechanical and viscoelastic properties of the material, such as the storage modulus (E', the elastic component of the material), loss modulus (E'', the inelastic component of the material), and tanδ or the damping factor.

Several testing modes are commonly used in DMTA, including:

i) ***Tensile testing:*** In this mode, the sample is subjected to a tensile load and the resulting strain is measured. The storage and loss moduli are calculated from the resulting data, and the tensile properties of the material, such as the tensile strength and modulus, can be determined.

ii) ***Single- and double cantilever testing:*** In this mode, the sample is clamped at one end and subjected to a sinusoidal load at the free end (single cantilever) or clamped at both ends and subjected to a sinusoidal load in the middle (double cantilever). The resulting bending motion of the cantilever is measured, and the storage and loss modulus can be determined from the data.

iii) ***Compression testing:*** In this mode, the sample is subjected to a compressive load and the resulting strain is measured. The compression properties of the material, such as the compression strength and modulus, can be determined from the data. This mode is particularly suitable for very soft materials such as soft elastomers or even hydrogels.

In conclusion, DMTA is a versatile technique that provides valuable information about the mechanical properties of materials, particularly viscoelastic behavior, as a function of temperature and frequency. It is widely used in the polymer and biopolymer industries to characterize the behavior of materials under various load conditions and to optimize the processing and use of materials.

5.6.Functional Characterization of Biodegradable Plastics

Giulia Fredi, Alessandro Pegoretti

5.6.1.Introduction

In addition to mechanical and thermal properties, the functional properties of biodegradable plastics, such as gas barrier properties, optical properties, antimicrobial properties, and biodegradability, are crucial for their successful implementation in various applications. Gas barrier properties determine the ability of the material to prevent the permeation of gases (such as oxygen and carbon dioxide) and water vapor, while optical properties can influence the appearance and functionality of the material. Antimicrobial properties, on the other hand, can enhance the safety and hygiene of the products made from these materials, while biodegradability is a key factor in ensuring their environmentally friendly nature. This chapter focuses on the methods for some of the most important functional characterization techniques of biodegradable polymers.

5.6.2.Gas- and vapor-barrier tests

Gas barrier properties are important for a wide range of applications, such as food packaging, where the shelf life of the product depends on the ability of the packaging material to prevent the permeation of gases, such as O_2 and CO_2, and water vapor. The gas and vapor permeability properties are essential for the successful implementation of biodegradable plastics in various industrial applications, as they can determine the shelf life of food products, the effectiveness of medical devices, and the durability of agricultural films. Therefore, the accurate testing and characterization of these properties are crucial for the development and optimization of these materials for specific applications.

Several international standards have been established for testing the gas and vapor permeability of materials. The most commonly used standards are ASTM D3985, ASTM F2476, and ASTM F1249. The ASTM D3985 standards provide a method for measuring the oxygen transmission rate (OTR) of materials estimated by oxygen permeability coefficients (OPC), which denotes the amount of oxygen diffusing through the film at a definite time and pressure per unit area of packaging film (kg mm^{-2} s^{-1} Pa^{-1}) (Katiyar et al., 2019). The ASTM F2476 and ASTM F1249 standards describe the test methods for carbon dioxide transmission rate (CO_2TR) and water vapor transmission rate (WVTR), respectively. Also, the ASTM E 96-95 standard test, known as the “cup method” is widely employed for evaluating the rate of water vapor permeability through plastic films (Katiyar et al., 2019).

These standards generally involve placing a known surface area of the material to be tested in contact with a controlled environment on one side, and a controlled carrier gas on the other side. The gas or vapor transmission rate is then calculated based on the measurement of the concentration change of the gas or vapor in the carrier gas over time, through different types of sensors (coulometric, infrared, etc.) (Li et al., 2020).

The OTR and CO_2TR values are important for food packaging, where the preservation of the food quality is crucial. For example, low OTR values can help to prevent the oxidation of food products, while low CO_2TR values can help to preserve the carbonation of carbonated beverages. The WVTR value is important for applications such as breathable films used in medical textiles or in agricultural films, where moisture regulation is important.

5.6.3.Testing of the optical properties

The optical properties of biodegradable polymers, such as transparency, haze, and color, are essential for many applications, the most immediate of which is the packaging field. Several international standards have been established for testing these properties, among which are ISO 13468, ASTM D1003, and ASTM E308. ISO 13468 provides a method for measuring the total luminous transmittance of materials, which is the ratio of the transmitted luminous flux to the incident luminous flux. ASTM D1003 describes the test method for haze measurement, which is the scattering of light within a material that results in a decrease in the transparency of the material. ASTM E308 provides guidelines for the instrumental measurement of color.

The testing of optical properties involves the use of specialized instruments such as spectrophotometers and colorimeters. For example, the measurement of transparency involves the detection of the light transmitted through a material, while haze is a measure of the amount of light that is scattered within the material, resulting in a decrease in transparency. The measurement of color involves the use of standard illuminants and observers. Color is an important property for many applications, such as in branding and the identification of products. The color of a material can be measured using various color scales, such as the CIELAB system (Ly et al., 2020), which measures the lightness, red-green, and blue-yellow values of the material.

The importance of these properties for industrial applications of biodegradable polymers and plastics is significant. For example, in food packaging, high transparency in the visible wavelength range (400-700 nm) and low haze values are essential to showcase the product and enhance its visual appeal. In the textile industry, the color of the material can determine its aesthetic appeal and its use in various applications.

5.6.4.Testing the antimicrobial properties

Antimicrobial properties are very important for several applications in the textile and packaging industry. Antimicrobial properties are divided into bacteriostatic festures, which inhibit the growth and reproduction of bacteria without necessarily killing them, and bactericidal features, which kill the bacteria by damaging the bacterial cell walls, disrupting their cell membranes, or interfering with their metabolic processes. In order to prolong the food shelf life, starch, cellulose, chitosan, pectin and other natural biopolymers have been widely used in active food packaging (Lei et al., 2021). There are several international standards that can be used for antimicrobial testing of biodegradable bioplastics, including ISO 22196, ASTM E2180, and JIS Z 2801. These standards outline the methods for determining the antimicrobial activity of materials by measuring the reduction of microorganisms over time.

Antimicrobial testing can be conducted using a variety of methods. The most commonly used method is the agar diffusion test, where a sample of the biodegradable bioplastic is placed onto a nutrient agar plate that has been inoculated with a known quantity of bacteria. After incubation, the diameter of the zone of inhibition around the sample is measured, which indicates the effectiveness of the bioplastic against the bacteria. The results of these tests can be used to determine the minimum inhibitory concentration (MIC), the rate of microbial growth, and the overall antimicrobial effectiveness of the bioplastic.

Testing antimicrobial properties is important for industrial applications of biodegradable bioplastics, especially in areas such as food packaging and medical devices. Biodegradable bioplastics with antimicrobial properties can prevent the growth of harmful bacteria, reducing the risk of contamination and infection. For example, biodegradable packaging films containing essential oils or other natural antimicrobial agents can extend the shelf life of fresh produce by inhibiting the growth of microorganisms that cause spoilage.

For example, Roy and Kim produced flexible and highly transparent PLA-based functional films with curcumin using a solution casting method. Curcumin was well-dispersed in the PLA matrix, and the composite film showed excellent compatibility with PLA (Roy and Rhim, 2020). The mechanical properties were slightly increased, and UV-barrier properties were excellent without sacrificing transparency. The addition of curcumin did not significantly affect the water vapor permeability or water contact angle of the PLA film. The PLA/curcumin composite film exhibited excellent antioxidant and antibacterial activity, making it suitable for active food packaging applications (Roy and Rhim, 2020).

Another example is that reported in the study by Lei et al. The study describes the preparation of catechol-functionalized chitosan (C-CS)/polyvinyl alcohol (PVA) composite films using a solution blending method in a neutral aqueous solution for active food packaging. The composite films showed a decrease in UV transmittance with an increase in C-CS content but still remained transparent in the visible range. The incorporation of C-CS into the PVA matrix improved the tensile strength and strain at break by 46.3% and 25.4%, respectively, compared to pure PVA, and the antibacterial properties of the composite films were also improved. Additionally, the water resistance of the films was not significantly impacted by the addition of C-CS. The results suggest that C-CS/PVA composite films have the potential for use in active packaging applications due to their good mechanical, antibacterial, and UV barrier properties (Lei et al., 2021).

In conclusion, antimicrobial testing is an important aspect of biodegradable bioplastic characterization and can provide valuable information on the ability of these materials to inhibit the growth of microorganisms. These properties are particularly important for food packaging and medical applications, where the prevention of contamination and infection is critical.

5.6.5.Biodegradability testing

Biodegradability is an important aspect to consider when evaluating the environmental impact of materials. This testing is performed to assess the extent to which these materials can be broken down by microorganisms into simpler substances such as carbon dioxide, water, and biomass, which can be further assimilated by the ecosystem or converted into valuable compost. As for the other characterization techniques, international standards for biodegradability testing have been developed to ensure consistency in testing methodologies and results. The most commonly used standards are ASTM D6400 and EN 13432. ASTM D6400 is a standard test method for the compostability of plastics, while EN 13432 specifies the requirements and test methods for the biodegradation and disintegration of packaging materials under industrial composting conditions. These standards require testing under controlled composting conditions, including temperature, moisture, and oxygen levels, and require the use of certified composting facilities.

Several methods are used to determine biodegradability in various environmental conditions, including carbon dioxide evolution analysis, respirometry, and monitoring of microbial activity. For example, respirometry measures the oxygen consumption rate of microorganisms that decompose the material. In this test, biodegradable plastics are added to a mixed microbial population under controlled conditions in a given environment (e.g., soil, compost, seawater, etc.), the rate of oxygen uptake is measured as a function of time, and the measurement is used to calculate the rate of biodegradation and mineralization of the bioplastic. The most important properties derived from biodegradability testing include the degree of degradation, the time taken for the material to degrade, and the products of degradation. These properties are crucial in determining the environmental impact of biodegradable polymers and plastics, and in identifying the most suitable materials for specific applications.

The importance of biodegradability testing for industrial applications of biodegradable polymers and plastics cannot be overstated. These materials are becoming increasingly popular as a more sustainable alternative to traditional plastics. However, without proper biodegradability testing, the environmental benefits of these materials may be limited or even negated. Biodegradability testing is necessary to ensure that these materials degrade effectively and do not persist in the environment as harmful substances.

5.6.6.Conclusions

In conclusion, the functional characterization of biodegradable polymers and plastics is essential to evaluate their performance and suitability for various industrial applications. Gas barrier properties are crucial for packaging applications to prevent the permeation of gases and water vapor, which can affect the shelf-life of the packaged product. Optical properties, including transparency, haze, and color, play a significant role in product aesthetics and consumer appeal. Antimicrobial properties are increasingly in demand for various medical and food packaging applications to prevent microbial growth and contamination. Biodegradability is also a crucial property to consider, especially for applications in the environment where biodegradable materials can provide an alternative to conventional plastics.

Highlights

- Microscopy-based techniques can be used to check for the structure, the presence of holes or imperfections and the degradation’ effects.
- Chemical characterization of biodegradable plastics can be achieved via XPS, ToF-SIMS, XRD, XRF, FT-IR and micro-RAMAN obtaining information on the structure or degradation.
- Mechanical characterization, including short- and long-term testing, is essential to ensure the performance and suitability of these materials for different applications.
- Factors affecting the mechanical properties include chemical structure, molecular weight, degree of crystallinity, processing conditions, and environmental factors.
- Thermal analysis techniques measure a material's response to temperature changes to determine its physical properties, crucial for the plastics and bioplastics industry.
- Biodegradable bioplastics with antimicrobial properties are important in industries like textile and packaging.

Interesting questions

- How does sample preparation affect the chemical and physical properties of polymers during characterization?
- What specialized techniques are required to analyze the different components of polymer blends or composites? How do differences in chemical structure and physical properties affect the analysis?
- How do the different mechanical characterization techniques, such as tensile, compressive, and flexural testing, provide information on the mechanical properties of biodegradable polymers and plastics?
- What are the key factors, at the molecular and microstructural level, that affect the mechanical properties of biodegradable polymers and plastics?
- How can the results from mechanical characterization tests be used to evaluate the suitability of biodegradable polymers and plastics for different industrial applications that involve different types of mechanical stresses?
- What is differential scanning calorimetry (DSC) and what are its advantages and applications in thermal analysis of biodegradable plastics?
- What is thermogravimetric analysis (TGA) and how does it help in understanding the composition, thermal stability, and degradation processes of biodegradable polymers?
- What are the testing modes and procedures involved in DMTA, and how do they contribute to the

understanding of the mechanical properties of materials, including viscoelastic behavior?

- What are the functional properties of biodegradable plastics besides mechanical and thermal properties?
- What are the methods and standards used for testing gas barrier properties of biodegradable plastics?

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CHAPTER 6: CURRENT APPLICATIONS OF BIODEGRADABLE PLASTICS

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6.1.Applications of Biodegradable Plastics in the Biomedical Field

Laura Pasquardini

The employment of biodegradable plastics in biomedical applications goes back to the 1960s, when they have been firstly used in the suture operation (Amass et al., 1998).

Different kind of biodegradable plastics can be used in biomedicine and are classifiable in three main categories, natural, semi-synthetic and synthetic, depending on the source and the production of these materials. Natural biodegradable polymers are derived directly from the natural sources like polysaccharides (chitosan, hyaluronate, cellulose, alginate and starch) or proteins (collagen, albumin or gluten); semi-synthetic are derived from nature but their polymerization is achieved through chemical modification like Poly(hydroxyalkanoate)s (PHA), polybutylene succinate (PBS) and Poly(hydroxybutyrate) (PHB), while synthetic biodegradable polymers are derived from chemical synthesis like poly(glycolic acid) (PGA), poly(caprolactone) (PCL), polyvinyl alcohol (PVA), poly(butylene succinate-co-adipate) (PBSA) and polyurethane elastomer (PU).

The requirements of these polymers for their application in the biomedical field are related to their mechanical properties, their biocompatibility, their biostability, their degradation rates and their processability. Depending on the application, they can be divided into two main categories, short or long-term devices and implantable devices.

The biodegradable polymer has to be selected keeping in mind its mechanism of degradation, that depends on the chemistry, the morphology and the molecular weight and also on the environmental pH or temperature at the place of insertion inside the body. The main degradation mechanisms are based on hydrolytic degradation, oxidation, or enzymatic degradation (Marin et al., 2013). The products of this degradation are non-toxic or are eliminated with minimal side effects even if the microenvironment can be affected by local reduction of pH.

In the following subparagraphs the biomedical applications of the different biodegradable polymers will be presented depending on their sources.

6.1.1.Biodegradable natural polymers

The biodegradable natural polymers used are mainly chitin, chitosan, starch, and silk.

The first use of chitosan as tissue repair goes back to 1988; later, it has been used in combination with different materials for antimicrobial application, as drug carrier for corneal lenses, in bamboo composite for guided bone regeneration and as templates for periodontal tissue regeneration (Vedula and Yadav, 2021). The use of nanofibers of chitosan has been also employed to increase the mechanical strength of cellulose scaffold, tuning in this way the water adsorption, the swelling, and the degradation capacity of the scaffold, and increasing the antimicrobial activity and enhancing the cell adhesion (Abutaleb and ArunPrasanna, 2022). Chitin nanofibril has been used in combination with nano-lignin and glycyrrhetinic acid for the production of electro-sprayed fibers with a strong anti-inflammatory activity for the cure of irritated complex skin wounds (Abutaleb and ArunPrasanna, 2022).

Silk sericin in combination with fibroin has been used to produce membranes, in alternative to collagen, for enhance the proliferation of adherent animal cells. They present an excellent oxygen permeability, like human cornea. Sericin can be used to produce polymer gels, membranes, foams, fibers, and other composite materials, obtaining materials with cryo-preservatives, anticoagulants, and biocompatible properties (Zhang, 2002). Due to its biocompatibility, biodegradability and non-immunogenicity properties, silk has been approved by Food and Drug Administration (FDA) for medical devices that include sutures and a support material during reconstructive surgery (Huang et al., 2018). Another field of application of silk is in tissue engineering: micro-structured and elastic silk hydrogels have supported stem cell growth and proliferation for greater than 3 weeks and aligned silk nanofibers have been successfully used for the regeneration of nerves. Moreover, silk-based nano and microspheres have been used as drug delivery systems (Huang et al., 2018).

Starch-based biodegradable polymers have been widely investigated in tissue engineering as bone cements that provide an immediate structural support and at the same time, degrade from the site of application. They can be loaded with bioactive agents useful to stimulate the bone regeneration. As microspheres or hydrogel these materials have been moreover used in drug delivery systems (Lu et al., 2009).

6.1.2.Biodegradable semi-synthetic polymers

The two main used biodegradable semi-synthetic polymers in biomedical applications are PHA and PBS.

PHAs polymers are distinguishable into three classes depending on the polymer chain: short, medium, or large. This length difference results into a different structural and mechanical property, but a common characteristic is their hydrophobicity. This feature has to modify in order to obtain a more hydrophilic system that is more compatible with biomedical applications (Hazer et al., 2012). One of the first studies on in vivo tissue responses to PHA polymers was by Baptist et al. (Baptist et al., 1965). Since then, applications in soft and hard tissues have been founded. In soft tissue engineering it has been used for sutures, wound dressing, cardiac patch, liver tissue regeneration, cartilage, and heart tissue regeneration; in hard tissue engineering it founded application as bone scaffold and implantable devices (heart valve, stent, nerve guidance conduit) (Hazer et al., 2012; Butt et al., 2018; Pulingam et al., 2022). Moreover, it has been used to build drug or carrier delivery systems. One drawback of the PHA-based devices is their production cost. the industrial and scale up of PHA-based material remains a big challenge.

To overcome this drawback a different semi-synthetic biodegradable material has been proposed, the PBS. It has a superior mechanical and thermal property, good processability, a high chemical resistance and a low cost of production. It has been successfully employed for the building of scaffolds for bone and cardiac tissue engineering, for drug delivery applications and as antimicrobial material (Gigli et al., 2016; Ostheller et al., 2022).

6.1.3.Biodegradable synthetic polymers

Biodegradable polyurethane elastomers are an important class of polymers that can be hydrolytically and enzymatically degradable and therefore find applications in the pharmaceutical or biomedical field. They exhibit good physic mechanical and antithrombogenic properties and good biocompatibility (Sobczak, 2015). Examples of these materials are already available on the market and the main biomedical applications are related to meniscal repair, ligament fixation and bone scaffolds, nerve and bone regeneration, catheter cuffs, antimicrobial materials, wound and nasal dressing, surgical sealant, stent coatings and drug eluting microspheres (Sobczak, 2015).

In a recent review, Grivet-Brancot and co-workers summarized the biomedical applications of PCL, PLA, PLGA, PUs, and their blends produced by fused deposition modeling (FDM), one of the most diffused 3D printing method, highlighting the critical aspects both on manufacturing and characterization (Grivet-Brancot et al., 2022). These systems have been successfully employed as scaffold, after proper surface functionalization, and another field that is growing in the interest is the building of tissues and organs on a chip, that are particularly relevant for drug screening and toxicology testing purposes. Organs on a chip rely on 3D printing in general for their implementation, since they usually combine bioprinting with 3D printing such as FDM to reproduce and sustain all the complexity of a physiological system. The main issue related to this field is the standardization of protocols and in silico analysis to obtain reliable results avoiding the use of animals.

For example, (ε-caprolactone) (PCL) polymer, alone or in combination with polyethylene glycol (PEG), has been approved by the FDA for many biomedical applications such as scaffolds, membranes, and sutures. Its use in thermosensitive hydrogels is particularly interesting as drug delivery injectable carrier and PCL-based nanofibers have been successfully used also in tissue engineering (Dethe et al., 2022). Due to its high mechanical strength, it can be used as polymeric scaffold for bone and periodontal tissue engineering; the slow degradation rate in vivo makes it an ideal material when a long-term stability is required.

The poly(glycolic acid) (PGA) was initially used for the production of sutures since it loses its mechanical stability in several weeks and then it is rapidly adsorbed by the body. Another field of application is related to the delivery of antitumor agents since the high biodegradability and biocompatibility of this polymer could efficiently deliver poorly soluble molecules or unstable reagents with low side effects and high drug loading efficiency. Moreover, it is used to produce screws, stents, and grafts for regenerative medicine applications and membranes (for artificial skin for instance) that can be naturally degraded in few weeks.

The last example of biodegradable plastic is PLA, that naturally degrades in situ through hydrolysis mechanism (Singhvi et al., 2019). The use of PLA-based materials in biomedical field, as material suitable for the direct contact with biological fluids, was approved in the 1970 by the FDA. It is widely employed in the biomedical field apart from its biocompatibility, also for its processability, in fact, it can be processed with a wide range of techniques (extrusion, injection molding, film and sheet casting, thermoforming, fiber spinning etc.). The material properties can be tuned adding suitable additives to improve its flexibility and processability. The material can be processed in different shapes, from implants to micro- and nanoparticles or nanofibers, for instance, it has been used in nanoparticles shape for drug delivery system or for imaging, in suture, stent, nerve regeneration, dermal fillers or tissue regeneration and many other fields.

Figure 6.1. summarizes the main biomedical applications of the biodegradable plastics both natural, semi-synthetic and synthetic ones. All these applications highlight the high biocompatibility that characterizes these materials and also the degradability. Based on the application required, in terms of long or short-term devices, the selection of the proper biodegradable plastic has to be performed: however, the choice can be made from a wide range of materials, as here reported, obtaining a proper bio-integration with the human body.

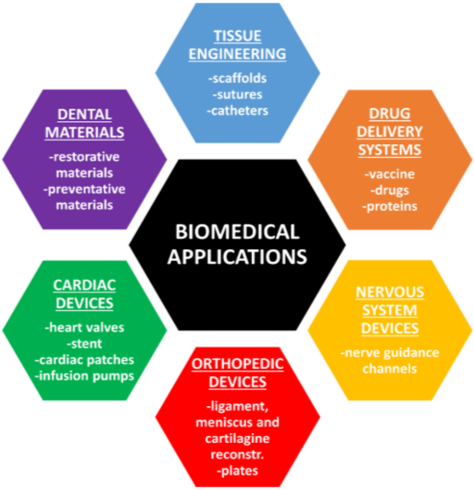

Figure 6.1. Biomedical applications of biodegradable plastics

6.2. Applications of Biodegradable Plastics in Agriculture and Horticulture

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Agriculture and horticulture are sectors where the use of biodegradable plastics is considerably expanding. Besides their biodegradability, some of the members of this polymer class offer supplementary advantages such as the elevated water uptake capacity, which can be useful to regulate the level of hydration of the fields. Biodegradable bioplastic products are used as mulch films, pots, seedbeds, and plant guides, but also for the controlled release of water and fertilizers and as traps for insects and microorganisms. The present Subchapter illustrates some of the uses of biodegradable bioplastics in agricultural applications, highlighting their advantages over their non-biodegradable counterparts.

6.2.1. Biodegradable bioplastics as mulch films

Mulching is a farming practice that aims at improving crop yield by covering the soil with specific films to prevent the growth of competitive plants (weeds) and to protect crops and soil by atmospheric agents that can dry up the ground, deteriorate fruits, cool the soil, and displace fertilizers.

Mulching is traditionally performed by applying various materials such as cardboard, gravel, straw, or plastic films. Although plastic films made of traditional, non-biodegradable plastic (e.g., HDPE) can be applied successfully for mulching, they must be withdrawn at the end of their service, with associated costs and the necessity for waste disposal. Conversely, biodegradable bioplastics can be left on the soil as they will naturally degrade under the action of atmospheric agents and soil microorganisms. It should be noticed that the selected biodegradable bioplastic must be able to biodegrade at a suitable time on the soil. If the degradation is too fast, the mulch film will not be able to successfully protect the crop and the soil, but if the degradation is too slow, there might be the necessity to remove the residual fragments from the soil at the end of the season, thereby raising the costs (Kuddus and Roohi, 2021).

Bioplastics have been proven very effective in this application, as they also contribute to reducing the nitrate loss and increasing the efficiency of water retainment and show higher water vapor permeability. On the other hand, the price of bioplastic mulch films is usually higher than those made of the non-biodegradable counterpart, but many governments subsidize their use, which contributes to increasing their application (Ashter, 2016). An example of mulch films made of biodegradable bioplastic is that made of Mater-Bi (Novamont, 2015), based on thermoplastic starch (Figure 6.2). Studies conducted by Novamont on such films highlighted that the material is biodegradable in a timeframe compatible with the agricultural cycle, and does not negatively impact soil quality, plants, and beneficial soil microorganisms (Bastioli, 2014).

Figure 6.2. Mulch film based on Mater-Bi (duplicated from (Novamont, 2015))

6.2.2. Biodegradable bioplastics for the controlled release of water and fertilizers

The increasing frequency of droughts caused by climate change is making irrigation systems more necessary in many regions (Thiery et al., 2020). However, in some areas, this type of irrigation is either very costly or not possible at all due to a lack of nearby water sources. To address this issue, some commercial plastic products have been developed to provide crops with water in a simpler way, such as Creasorb by Evonic or Luquasorb by BASF. These materials can absorb a significant amount of water during rainy periods, even when these are scarce, and then slowly release it to meet the needs of the plants. However, these plastics can only be used once and must be removed to prevent the transfer of toxic substances to food products, which incurs additional costs. Bioplastics can be a solution to this problem. Some of these bioplastics, for example Xanthan gum, can be considered superabsorbent, capable of retaining more than 1000% of their weight in water without disintegrating (Cuadri et al., 2017). These superabsorbent bioplastics can capture water in the same way as traditional plastics, but release it as they biodegrade, so they don’t have to be removed from the crop at the end of their use. As a result, these systems are becoming increasingly popular in the agriculture sector. Researchers are currently investigating different types of bioplastics to maximize their absorbent capacity without compromising their mechanical properties and biodegradability, in order to provide sustained water for crop growth.

Another application of bioplastics in agriculture is the controlled release of fertilizers. The use of excess fertilizers in crops can cause damage to subsoil and groundwater, leading to increased research in alternative methods such as conservation tillage and reducing the use of anthropogenic residues. However, these alternatives are not as effective as fertilizers in improving crop growth. This has led to the development of systems for the controlled release of fertilizers to match the needs of crops and increase the efficiency of nutrient assimilation, reducing pollution (Kuddus and Roohi, 2021).

Industrial plastic systems for controlled release of fertilizers such as Nutricote® by Projar Group (Valencia, Spain) and Multicote™ by Haifa Haifa Negev technologies LTD (Israel) have been commercialized, however, these systems also face challenges due to the low biodegradability of the plastics used, which can remain in the soil and be difficult to remove. Bioplastic matrices are becoming an attractive alternative in this application as they can hold fertilizers as a filling material and release them in a controlled manner through irrigation water or through biodegradation of the matrix. This improves fertilizer efficiency and eliminates the problem of removing the systems since they degrade into non-toxic products for cultivation (Karan et al., 2019). Studies have been conducted to evaluate the proportion of different nutrients that can be incorporated into bioplastic matrices, and also how to adjust the kinetics of nutrient release to the needs of different crops, to obtain more specialized fertilization and improve crop yields (Jiménez-Rosado et al., 2020).

6.2.3. Other applications of biodegradable bioplastics in agriculture

Finally, other interesting applications of biodegradable bioplastics in agriculture are as traps for insects and microorganisms and as seedbeds or biodegradable pots. Bioplastics can be utilized as traps for insects and microorganisms to reduce the need for pesticides in organic crops and prevent damage to plants caused by the use of toxic substances. Natural substances with attractive odors, such as imidacloprid, are often added to bioplastics to make the materials more attractive to these organisms (Singh et al., 2020). These substances are released in a controlled manner through the biodegradation of the bioplastics, allowing the traps to remain effective for an extended time.

Furthermore, bioplastics can be used as seedbeds and plant guides, which do not need to be removed after use and avoid problems associated with cutting or damaging the roots or stems of crops (Mosnáčková et al., 2019).

However, for these applications, and those previously mentioned, bioplastics must maintain good mechanical properties throughout their use, which can be impacted by their biodegradability. Therefore, a thorough study of all conditions is necessary for optimal use.

6.3.Applications of Biodegradable Plastics in the Packaging Field

Giulia Fredi, Alessandro Pegoretti

6.3.1.Challenges and opportunities for biodegradable plastic packaging

As previously discussed, biodegradable polymers are not a simple replacement for traditional plastics. They must be viewed as an opportunity to redesign applications with an emphasis on the efficient use of resources and the elimination of waste. To be successful, this requires a systemic approach that transforms local issues into business opportunities and shifts away from the management culture that has contributed to the current dissipative growth model. The efficient use of resources is the fundamental criterion needed to avoid aggravating the current situation and reversing the trend toward a more sustainable future. This can be achieved through a cascading model of growth that prioritizes the territory and knowledge economy and eliminates waste and rejects. To accomplish this, standards must be selected that go beyond products and focus on systems. The goal should not be to maximize market volumes but to promote local regeneration from an environmental, social, and economic perspective, and encourage a cultural shift towards a system-based economy. To achieve this in the plastic value chain, industries and institutions should select stringent quality rules to guarantee: **i)** compostability and biodegradability in different environments, **ii)** nontoxicity of products, **iii)** a low environmental impact for the whole product life cycle, and **iv)** a continuous improvement program in terms of the quality of raw materials, renewability level, production chain, in-use efficiency, and end-of-life options (Bastioli, 2014).

One of the applications for which this shift is more urgent is the packaging field. Biodegradable plastics, like conventional plastics, offer a wide range of packaging applications. Some options include bags for compost, agricultural foils, horticulture, nursery products, toys, and textiles, as well as packaging for contact articles including disposable cutlery, drinking cups, salad cups, plates, overwrap, and lamination film, straws, stirrers, lids and cups and containers.

Among the most interesting and challenging fields for packaging is that of perishable items such as food, because this application combines the short shelf life, associated with high disposal demand and high mechanical, optical, and functional requirements. In food packaging applications, biodegradable plastics must protect the food from the environment as well as, maintain food quality. To achieve this, it is important to control and modify the mechanical and barrier properties of the biopolymer, and to study the changes in properties of the packaging material during its contact with food (Ashter, 2016). The next two subchapters will focus on the application of biodegradable bioplastics in food packaging.

6.3.2.Biodegradable food packaging

The use of biodegradable plastics in food packaging is becoming increasingly important as consumers demand more eco-friendly and safe packaging options. Traditional synthetic polymers, while effective in protecting food from spoilage and contamination, present disposal problems due to their non-biodegradable nature. On the other hand, biodegradable or compostable polymers offer a viable alternative as they can effectively solve the problem of waste accumulation, provided that they are correctly disposed (Tawakkal et al., 2014)

Food packaging plays a crucial role in protecting and preserving food items, communicating with consumers, and facilitating storage and distribution. In recent decades, the demand for ready-to-eat foods has grown, requiring the development of convenient packaging that can withstand microwave heating and minimize product handling. Biodegradable polymers such as starch, cellulose, chitosan, PLA, PCL, and PHB have been developed as an alternative to synthetic polymers for food packaging. These materials can be processed into various forms such as films, laminated paper, trays and cups, and cutlery items, depending on the production method used (Yadav et al., 2018; Katiyar et al., 2019).

The demand for biodegradable polymers has been increasing at a rate of 20-30% annually, but it still represents less than 0.5% of total plastic use in the market. Despite this, with increasing concerns over plastic waste, researchers and food processors must continue to explore the potential of biodegradable polymers to meet consumer demands for sustainable packaging options (European-Bioplastics, 2021).

6.3.3. Active food packaging based on biodegradable bioplastics

Biodegradable bioplastics such as PLA, PHAs, and TPS can be the basis for the production of active food packaging, i.e., packaging including additives that retain or expand product quality or shelf-life. For example, these polymers can be blended with active molecules such as chitosan, essential oils, and plant extracts to create packaging that actively fights against microorganisms and slows down the oxidation process, preventing food spoilage. These natural compounds are environmentally friendly and safe to use in food packaging, offering a sustainable alternative to traditional preservatives. Some of the most common active agents are presented in Figure 6.3.

Additionally, biodegradable polymers can be designed to degrade in specific environments such as in compost, reducing the environmental impact of packaging waste. Overall, active food packaging using biodegradable polymers presents an opportunity to improve food sustainability and safety while reducing packaging waste

(Vilela et al., 2018). The following subchapters focus on the development of active packaging based on three major biopolymer classes, i.e., PLA, PHAs, and TPS.

Figure 6.3. Active agents for food packaging (duplicated from (Vilela et al., 2018)).

6.3.3.1.PLA- and PHA-based active packaging materials

Biodegradable polymers, such as PLA and PHA, are gaining traction as sustainable alternatives to traditional plastics in food packaging applications. One of the ways they can be used is as a carrier or matrix for active agents that provide controlled and sustained release of antimicrobial or antioxidant properties to the wrapped or packed food, extending its shelf life and protecting it from spoilage. Natural additives are often added to these polymeric matrices for reinforcing or adding specific properties, such as the use of herb extracts or essential oils. Recent studies have shown the potential for using PLA and

PHA-based films infused with these bioactive agents, such as fennel or ginger oil, for preserving food items like oysters and peaches. Additionally, incorporating other agents, like propolis extract and PEG/$CaCO_3$, can further enhance the effectiveness of these active films while also improving their flexibility and stiffness (Kuddus and Roohi, 2021).

For example, in a study conducted by (Jiang et al., 2020), films made of blends of PLA and P3,4HB, which were obtained by melt blending, were loaded with ginger and angelica essential oils as a means of preserving peaches. The aging and spoilage of the peaches were monitored using Low-Field Nuclear Magnetic Resonance (LF-NMR) method, and it was found that the films containing angelica essential oil resulted in the best preservation effect. The proton density map of this group (PLA-P3,4HB-AEO) was observed to be light blue in color, indicating a prolonged shelf-life for the peaches treated with this type of film. The research suggests that the films containing angelica essential oil effectively delayed the oxidation of peaches and maintain the combined water, resulting in a shelf life extended by more than 15 days.

6.3.3.2.Active food packaging containing TPS

Another material that has been widely studied in this field is thermoplastic starch (TPS), as it offers a range of benefits such as high resistance to water and gas transfer and good oxygen barrier properties. Multilayer materials containing TPS are a practical solution for reducing food spoilage (Kuddus and Roohi, 2021).

One strategy that has been explored is blending TPS with other polymers, such as PLA. This combination allows for the retention of moisture resistance and good mechanical properties in TPS, while also incorporating the flexibility and oxygen resistance of PLA. For example, Nawab et al. investigated the use of mango kernel starch as a coating for tomatoes, finding that it was a natural and effective way to extend the shelf-life of the fruit (Nawab et al., 2017). Similarly, Sanyang et al. prepared bilayer films from sugar palm starch and PLA, resulting in a material with good mechanical and water barrier properties (Sanyang et al., 2016).

Another approach is to incorporate antimicrobial agents into TPS matrices to improve the quality of food products. (Campos-Requena et al., 2017) developed nanocomposite films made from starch, clay, and essential oils that were found to be effective in extending the shelf-life of strawberries. Similarly, (Medina-Jaramillo et al., 2017) synthesized active biodegradable films from cassava starch and natural extracts like green tea and basil, while (Romani et al., 2017) evaluated the use of oregano essential oil in rice starch/fish protein active packaging films. Chitosan has also been found to be a suitable antimicrobial agent for TPS packaging materials (Mendes et al., 2016).

Overall, TPS-based active food packaging materials are a promising area of research, providing a natural and eco-friendly alternative to traditional packaging methods while increasing the shelf life of food products.

6.3.4.Conclusions

There are a number of challenges and opportunities associated with biodegradable plastic packaging. One of the main challenges is cost as biodegradable plastics are generally more expensive than traditional plastics. This may limit the extent to which they are adopted, particularly in highly price-sensitive packaging applications. Additionally, biodegradable plastics may not perform as well as traditional plastics in certain applications, particularly for lower durability and barrier properties. Another challenge is consumer education, as the public may not understand the difference between biodegradable and compostable plastics and may not know how to properly dispose of them. This can lead to confusion and potential contamination of recycling streams.

Opportunities for biodegradable plastic packaging include the potential for increased sustainability, as well as the ability to reduce waste and pollution. Additionally, with increasing government regulations and consumer pressure for more sustainable packaging options, there is likely to be a growing demand for biodegradable plastics in the packaging industry. Furthermore, advancements in biodegradable plastic technology may improve the performance and reduce the cost of these materials over time, making them more viable options for a wider range of packaging applications.

6.4. Applications of Biodegradable Plastics for Consumer Goods

Giulia Fredi, Alessandro Pegoretti

6.4.1. Biodegradable electronics and electronic devices

The use of biodegradable bioplastics in the consumer electronics sector has seen significant growth in recent years. The plastics used in casings, circuit boards, and data storage are sought after for their durability, toughness, lightness, and mobility. However, bioplastics are increasingly being used as an alternative in the production of consumer electronics. These bioplastics are being utilized in a wide range of products, including touchscreen computer casings, speakers, keyboard elements, mobile casings, vacuum cleaners, and laptop mice. Companies like SUPLA have developed optimized compounds based on lactides from Corbion Purac for use in the consumer electronics industry. The world's first bioplastic touchscreen computer, developed in collaboration with a Taiwanese OEM/ODM, Kuender, is a notable example of this innovation. The high gloss housing of the computer is made from PLA and the blends used for the monitor screens improve impact resistance, provide an excellent high gloss finish, and stable, precise processing. Other examples of biodegradable consumer electronics include computer keyboards, earphones, mobile phones, laptops, game consoles, and tablets (Ashter, 2016).

Another exciting field where biodegradable biopolymers can give a remarkable contribution is that of biodegradable elastic electronics. As described in a recent paper by Chen et al. and illustrated in Figure 6.4, biodegradable flexible electronics have a high potential for electronic-waste management and sustainable development, as well as for biomedical applications of implantable transient electronic devices (Chen et al., 2022). The biodegradable elastomeric materials, which have been recognized as a key to driving this field, will have a wide impact on a range of fields including biomedical engineering, wearable electronics, and soft robots.

Figure 6.4. Illustration of stretchable biodegradable electronics, exhibiting the two fabrication strategies and the required mechanical properties. Duplicated from (Chen et al., 2022).

There are currently two main strategies for creating elastic electronic devices: structure-based and material-based. The structure-based approach involves constructing patterns, such as fractals and serpentines, of non-stretchable conductive materials on substrates to enhance strain tolerance. However, this method may result in a mismatch between the rigidity of the traditional electronic materials and human soft tissue. On the other hand, the material-based approach focuses on the preparation and processing technologies of intrinsically stretchable materials, such as elastomers and gels, in order to endow intrinsic elasticity to individual device components and their integrated systems. Inorganic nanomaterials and conjugated polymers are commonly used as electronic fillers to be combined with biodegradable elastic polymers to create percolation networks that allow for continuous movement of carriers even under stretching, leading to a combination of conductivity and elasticity. Polymers can be processed by common methods like molding, spinning, 3D printing, and micro/nano fabrication to create integrated elastic electronic devices.

Therefore, the focus of this research field is on biodegradable conductive and semiconductor elastomers and biodegradable hydrogels. Typical elastomers used for this application are polyglycerol sebacate (PGS), PGS derivatives, poly(1,8-octanediol-co-citrate) (POC), urethane-based elastomers, and dynamically covalent crosslinked elastomers; typical hydrogels are based on polysaccharides (e.g., cellulose, chitosan, alginate) and protein-based polymers (e.g., silk, gelatin). The main challenge in developing such materials is to find a good balance between biodegradability, mechanical properties, and electrical conductivity (Chen et al., 2022).

6.4.2.Automotive

The automotive industry is looking for ways to lower fuel usage and decrease CO_2 emissions, one approach being the reduction of vehicle weight. This presents a chance to expand the usage of bio-based and/or biodegradable polymers in the sector. Many leading car brands have already adopted the use of bio-based plastics such as bio-based polyamides and polyesters as a way to decrease their environmental impact. These bio-based polymers have all the necessary properties to be used in high-quality car components, such as bio-based coatings for interiors or exteriors, fiber reinforced thermosetting polymers, shape memory polymers, and piezoresistive components for prototypes. Composites made from bio-based polymers are also a popular choice for their good mechanical properties and ease of combination with other materials. These composites can be used in structural parts of the vehicle such as door handles, dashboard fascia, and panels. There is ongoing research and development of new materials, including biodegradable plastics, with well-defined properties to meet both service and environmental needs. Additionally, 3D printing technology is becoming a popular method in the industry for rapid prototyping and industrial production of high-value products like luxury cars. This growth in 3D printing also leads to an increase in the use of bio-based and/or biodegradable polymers like PLA, PCL, or PHAs (Ashter, 2016).

6.4.3.Food services

The convenience of taking food and beverages to go has become a common aspect of modern living. In Germany, for instance, the catering industry, including items such as plastic utensils and dishes, paper, and cups, has a market volume of around 3.5 billion Euros and has grown by an average of 7% annually over the past decade. However, recent political initiatives by the European Commission for more sustainable options in the single-use segment have sparked a reevaluation of the industry. Despite this, the need for a balance between disposable and reusable options must be maintained in order to ensure food safety and hygiene. To meet this demand, a wide range of bioplastics products are available for the food and catering industry, including cups, mugs, trays, plates, and utensils in both disposable and reusable forms. Single-use products are still necessary in certain situations, particularly in closed systems with integrated waste management such as on airplanes, at sporting events, or in correctional facilities (European-Bioplastics, 2021).

6.4.4.Other consumer goods

Biodegradable polymers are widely used in consumer goods products, such as furniture, suitcases, grinding discs, and safety helmets. These products often utilize natural and bio-based composites, like cellulose fiber and PLA blends. Additionally, these polymers are commonly utilized in adhesives, paints, engine lubricants, and construction materials. Biodegradable golf tees and fishing hooks have also been developed using these materials. One example is cellulose acetate, which is used in the production of toothbrush handles and adhesive tape. Starch-based materials are also finding new applications, such as in coffee capsules. WillowFlex, a new material that is currently being tested, has the potential to be used for the manufacturing of toys using 3D printing. Another material, SEPPA, made from marine shells by Chieng Roung Industry, is also used for biodegradable toys like Lego-like blocks, plastic balls, toy models, pens, and art knives (Torres-Martínez et al., 2019).

6.5.The Others - Environmental and Nanotechnology Applications

Cem Gök

Due to its growing population and desire to match rising standards of life, it has experienced rapid urbanization and industrialization, which has had a significant impact on the global economy for many years. The idea of having a sustainable and advanced economy not only drives the development of various technological solutions, but also creates ongoing demands on natural resources, such as the production of biopolymeric materials that have an adverse effect on the environment due to their large-scale production. Sustainable research methods are used to study production procedures and the removal of post-use waste. These factors, along with biopolymers' biological degradability and biocompatibility, have caused them to garner interest from a wide range of study fields. These characteristics of biopolymers, when compared to other conventional or traditional materials, have made them a possible choice for many applications, and they are currently the subject of extensive research such as wastewater treatment, tissue engineering, nanotechnology, food industries, biosensor and photovoltaics, drug delivery, nuclear applications and so on (Gok and Aytas, 2013; Gok et al., 2013; Gok and Aytas, 2014; Mohan et al., 2016; Smith et al., 2016; Mohiuddin, 2017; Özcan et al., 2022, Özdil and Özcan, 2023).

Nanotechnology, known as the science of nanomaterials, is related to the production, characterization, and application of these materials. The creation of more environmentally friendly methods to create nanoparticles is a current research priority. The synthesis procedure now places a greater emphasis on "green" chemistry and bioprocesses than it did on physical and chemical processes. Due to the influence of quantum size, nanoparticles have a variety of new features. Yet, a significant environmental concern is posed by the majority of their synthesis technique. When creating diverse nanoparticles, biopolymers can be utilized in their place, such as chitosan, starch, heparin, cellulose, poly(vinyl alcohol), gelatin and others, to substitute harmful chemicals (Mohan et al., 2016; Oztürk et al., 2020).

The term nanocellulose, which can be given as the best example of nanotechnology applications of biopolymers, is used to describe nano-structured cellulose.

Nanocellulose can be obtained from both bacteria and cotton linter by chemical processes. With environmental approaches, simple and economical processes, it is possible to produce cellulose nanocrystal and cellulose nanofibers. Attributing biodegradability and biocompatibility without toxicity, both derivatives are valued for promising application potential in many industries. Silk, alginate, keratin, gelatin, collagen, fibroin, corn zein and soy protein, chitosan has been used in nanoparticle research studies, including drug delivery and biomedical fields. Biopolymer nanoparticles hold promise in applications for cancer therapy and diagnosis due to their tumor targeting capabilities and selectivity (Chaabouni et al., 2013; Isıtan et al., 2022).

Environmental conditions have deteriorated dramatically and alarmingly as a result of the introduction of natural or manmade pollutants. There are many different kinds of environmental contaminants that are bad for both the ecosystem and people’s health. The most prevalent pollutants that result in impacts including genetic mutation, gastrointestinal dysfunction, birth defects, neurological diseases, conjunctivitis, and allergic reactions are heavy metals, dyes, pesticides, and surfactants (Yaashikaa et al., 2022). Many studies in this field in recent years have focused on the ability of biopolymers and their composites to remove impurities via adsorption method.

Biosorption, subcategory of adsorption, is a property of biomaterials as biopolymers and bio composites to bind, concentrate and remove contaminants, even from very dilute aqueous solutions. Many biopolymers, including certain fungi, cellulose, alginate, and chitosan, are known to firmly bind pollutants, and could be employed in biosorption. Biopolymers are extremely competitive with ion-exchange resins and activated carbon because they are nontoxic, selective, functionality, availability and abundance, low cost and renewability, biodegradability, ease of functionalization and modification for effective sorption properties. Because biomass has a wide range of structural elements, numerous functional groups, such as carboxyl, phosphate, hydroxyl, amino, and thiol, can interact with pollutants in varying degrees and are influenced by physicochemical parameters. Sorption, ion exchange, and complexation/coordination mechanisms may be crucial for biosorption, which is defined as a physicochemical process independent of metabolism. In these circumstances, biosorption can be quick and reversible with biomass having properties similar to those of traditional ion exchange resins (Gok et al., 2013; Gok and Aytas, 2014).

One of the interesting applications of biopolymers is the use of Ca-alginate biopolymer beads to reduce the bioavailability of radionuclides in the gastrointestinal tract of humans. Internal contamination due to acute or chronic exposure could result in both radiological and chemical harmful consequences in the event of an accidently released actinide in a nuclear site or the environment. Any radioactive material that is consumed will enter the digestive tract and be treated like any other element, whether it was ingested primarily through contaminated food and drink or secondarily through the respiratory system. Using in vitro methods, the removal of strontium, uranium, and thorium from a gastrointestinal tract was investigated. According to the egg-box model, this agent was created from Na-alginate by cross-linking it with divalent calcium ions. The Schematic representation of the egg-box model and scanning electron microscope (SEM) of Ca-alginate can be seen in Figure 6.5. For the purpose of removing radionuclides from the gastrointestinal juice, the impacts of process variables including incubation time, solid-to-solution ratio, and pH of the gastrointestinal juice were examined. The findings imply that this material is an effective substance for lowering the bioavailability of radionuclides with high gastrointestinal absorption efficiency (Gok et al., 2013).

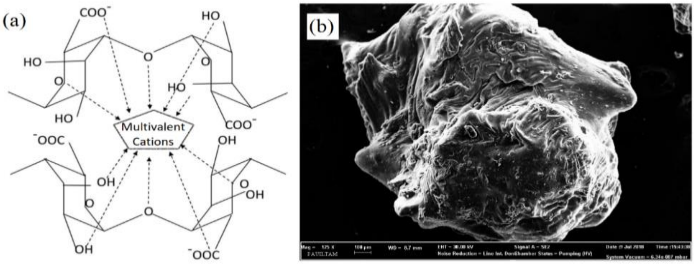

Figure 6.5. Schematic representation of the egg-box model (a) and scanning electron microscope (SEM) image (b) of Ca-alginate biomaterial.

Highlights

- The biodegradable plastics has to be selected having in mind the application and the site of insertion in the body,
- The mechanical properties, the biocompatibility, the biostability, the degradation rates and the processability are key parameters,
- Short or long-term devices and implantable devices can be made of biodegradable plastics,
- Biodegradable bioplastics can be used in farming as mulch films, which increase crop production by covering the soil and preventing weed growth while also protecting crops and soil. Traditional plastic mulch films must be removed when they no longer serve their purpose, while biodegradable bioplastics can be left on the soil to degrade organically.
- Water and fertilizer can be released in a regulated manner using biodegradable bioplastics. During rainy seasons, they can absorb a substantial amount of water and then gradually release it to suit the needs of the plants. This is becoming more common in agriculture as researchers examine several types of bioplastics to enhance their absorbent capacity while maintaining mechanical qualities and biodegradability.
- Biodegradable bioplastics can potentially be used to regulate fertilizer release in agriculture. They can be designed to release nutrients at a controlled rate, allowing for more efficient fertilizer use and reducing negative environmental impacts.

- Biodegradable polymers are not a straightforward replacement for traditional plastics; they necessitate a comprehensive approach to redesigning applications with an emphasis on resource efficiency and waste minimization. This necessitates a cascade growth paradigm that prioritizes the territorial and knowledge economy while eliminating waste and rejects.
- One of the most challenging and exciting fields for biodegradable polymers is packaging. Biodegradable plastics can be found in a variety of packaging applications, including compostable bags, agricultural foils, horticulture, nursery products, toys, and textiles, as well as packaging for contact articles such as disposable cutlery, drinking cups, salad cups, plates, overwrap, straws, stirrers, lids, and containers.
- Biodegradable food packaging is growing more popular as consumers want more environmentally friendly and safe packaging solutions. If properly disposed of, biodegradable or compostable polymers can efficiently tackle the problem of trash accumulation. Food packaging is essential for protecting and keeping food, connecting with customers, and enabling storage and distribution. Biodegradable polymers such as starch, cellulose, chitosan, PLA, PCL, and PHB have been used to replace synthetic polymers in food packaging, however they must be able to manage and adapt the mechanical and barrier properties of the biopolymer.
- Biodegradable bioplastics are being employed as an alternative to regular plastics in the consumer

electronics industry. They are used in a variety of items such as touchscreen computer casings, speakers, keyboard elements, mobile casings, vacuum cleaners, and laptop mouses.

- Biodegradable elastic electronics are an intriguing subject in which biopolymers can play a big role. Biodegradable elastomeric materials have a strong promise for electronic waste management and sustainable development, as well as for implantable transitory electronic device biomedical applications. This study topic is primarily concerned with biodegradable conductive and semiconductive elastomers, as well as biodegradable hydrogels. Finding a reasonable balance between biodegradability, mechanical characteristics, and electrical conductivity is the key problem in producing such materials.

Interesting questions

- How can biodegradable bioplastics be optimized for use as mulch films in agriculture?
- What are the most promising applications of biodegradable bioplastics in controlled release irrigation and fertilizer systems in agriculture?
- How can the use of biodegradable bioplastics in agriculture be incentivized and scaled up?
- How can biodegradable bioplastics be optimized for use in packaging applications, especially in the food packaging field?
- What are the most promising applications of biodegradable bioplastics in packaging?

- How can the use of biodegradable bioplastics in packaging be incentivized and scaled up?
- What are the main applications of biodegradable bioplastics in the consumer goods market?
- How can biodegradable bioplastics be optimized for use in the consumer electronics sector?
- What are the most promising applications of biodegradable bioplastics in the field of biodegradable elastic electronics?

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CHAPTER 7: IMPACT OF BIODEGRADABLE PLASTICS: MARKET TRENDS FOR BIODEGRADABLE PLASTICS

Graţiela Dana Boca

7.1.Importance of Biodegradable Plastics

Graţiela Dana Boca

Despite growing mistrust, plastic is essential to modern life. Plastic materials have been the basic material in the new field of computers, generations of high-performance mobile phones, but also in the field of modern medicine. Without plastic, it can be assumed that many products are within everyone's reach. The increase in demand for products led to the appearance of plastic, which resulted in the appearance of cheaper, lighter, safer and stronger products, but which currently represent a danger and require replacement with biodegradable materials.

As it is clear that plastic has a valuable place in our lives, scientists are trying to make plastic safer and more sustainable. The new innovations led to the discovery of bioplastic that degrades over time because they have as raw material plants being more ecological than conventional plastic.

Scientists are looking for innovative solutions, ways to make plastic recycling more efficient and even hope to perfect a process that turns plastic back into fossil fuels.

Plastics are not perfect, but they are ubiquitous, they make our lives art, so humanity need to find a solution for the future.

Although the term “bioplastic” sounds futuristic or science fiction it actually represents the future. The first artificial plastic was introduced in 1862 and was a bioplastic, meaning it was made from a renewable resource.

Bioplastics can be **bio-based** (produced from a renewable resource), **biodegradable** (capable of decomposing naturally) or both. Biodegradable bioplastics can be just as durable as other types of plastic because they only break down under specific conditions. They can be made from renewable raw materials or from natural plant or animal materials, such as orange peels, corn oil, grass, soybeans, microorganisms or starch. The industrial processing of biodegradable plastics is similar to the manufacture of ordinary plastics, only the materials used differ for biodegradable plastics; are the materials that can decompose or decompose easily. It can be identified as two categories:

i) Bio-plastic produced from natural materials causes a decrease in energy consumption and less carbon emissions, since the plants used already contain the same amount of carbon.

ii) Biodegradable plastic material; which is based on oil, but which decomposes faster due to the presence of additives that accelerate the degradation in the presence of oxygen, light and moisture by accelerating the decomposition process. Most bioplastic is used in single-use packaging or shopping bags can be composted at home. But at the same time, industrial composting is done on a much larger scale than home composting and requires more active management than home composting.

7.2.Why are Bioplastics so Important?

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They are made from renewable and/or biodegradable resources, which can help reduce dependence on fossil fuels, support sustainability initiatives and allow manufacturers to diversify raw materials. While bioplastics have been touted as the savior of the world’s plastic pollution problems, bioplastics also have some problems of their own. Bioplastics are made, at least in part, from plants. This means that the land must be used to grow the plants that are used. They are also frequently made from plants such as corn, which are often grown as a monoculture, which is not as beneficial for the environment as growing with more diversity. Also, bioplastics must be disposed of with appropriate techniques. If we pay attention to plastic evolution we can identify different stages of awareness regarding plastic, waste plastic and management plastic became a priority (Figure 7.1).

In 1862 at the Great International Exhibition in London Alexander Parkes demonstrated his invention “Parkensine” which was an organic cellulose-based material. It was the year of revolutionary plastics production.

Pollution emerged in the 1960s, when the first bag was discovered in Ireland, highlighting the environmental problems facing humanity. With the development of technology and the existence of plastic waste, the problem of environmental protection has also gained importance.

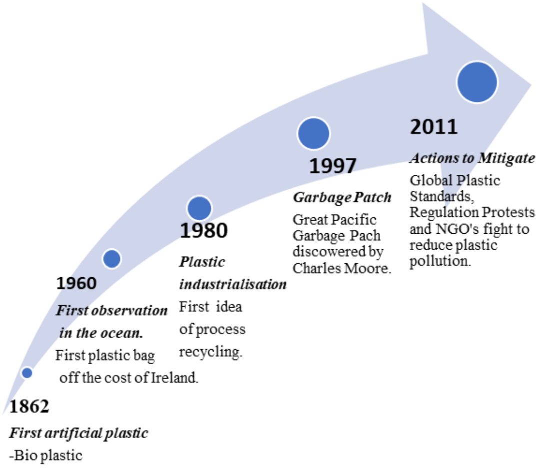


Figure 7.1. Plastic in time from pollution to awareness evolution

The problem that existing plastic disappears is provided by time and a number of techniques, but also brings with it some problems such as bioplastics, recycling and landfilling.

The unmistakable optimism about plastics did not last long. In the post-war years there was a change in perception as plastics were no longer viewed positively. Initially, plastic represented a solution, but over time, its excessive use in different areas led to plastic pollution of the oceans and the environment.

Plastic’s reputation declined further in the 1970s and 1980s; Plastic has become a particular target because plastic remains in the environment indefinitely. In the 1980s, the plastics industry attracted municipalities to collect and process recyclables as part of their waste management systems. Even if recycling is carried out, it was far from perfect, because plastic materials still ended up in landfills, which is still a problem now. Plastic represented a danger to human health, but at the same time there was a danger of chemicals leaking from plastic into food, water, and bodies. In 1997 a yachtsman Charles Moor discovered the Great Pacific Garbage Pach (floating plastics bottles and other debris) which was an alarm signal about the pollution and environment sustainability. In 2011, actions to mitigate plastic began by implementing global standards specifically for plastic, regulations that use plastic symbols, and the implementation of the 3Rs, which have slowly become the norm.

7.3.Challenges of Using Biodegradable Plastics

Graţiela Dana Boca

Most people are familiar with plastic products, and those who are passionate about the bioplastics industry with a scientific and technical background are trying to communicate the benefits of bioplastics to the uninformed and non-technical public. It is important that the changes come together with new types of plastic so that people are convinced by these changes. The perception of plastic and biodegradable materials has changed by harmonizing with international standards.

Rujnić-Sokele and Pilipović mention the concept that materials originating from nature with ecological advantages of being biodegradable (bioplastics) is very attractive for industry and consumers (Rujnić-Sokele and Pilipović, 2017). Bioplastic is already used in the field of packaging, agriculture, gastronomy, consumer electronics and in the automotive field.

The future opportunities and challenges of biodegradable plastics are in terms of processing, properties, and waste management options. Ren (2003) though developed as a solution for the waste problem, biodegradable plastics create new challenges on waste management with respect to policies and laws, waste management technologies and application of market-based instruments. In the framework of the waste management system with biodegradable plastic materials, emphasis is placed on the regulatory aspects as well as the economic ones. Waste management is the collection, processing, treatment, and recycling of waste.

The Waste Management process goes through several stages: storage, transport, treatment, and disposal of waste; monitoring, overseeing, and regulating development, processing, transit, treatment, and disposal for the better health of our environment.

Waste control or disposal represents the totality of actions required to handle waste from the time of collection to final disposal. This stage includes the storage, transport, management, and recycling of waste, but also the control and application of standards.

The standards have been harmonized with the legislative and regulatory system for waste control, including recycling guidelines, etc.

The most popular types of Waste Management are Recycling, Incineration, Landfill, Biological Reprocessing and Animal Feed.

7.4.What To Do with Waste?

Graţiela Dana Boca

The recycling procedures are pretty much the same for all types of plastic waste. In the case of PETs, they arrive at specialized collection units, from companies that generate large volumes of such packaging or through our own collection operations. PET waste enters a conveyor belt, where it is cleaned, then sorted by color, after which it enters the grinding-washing line, where it is chopped, repeatedly washed and dried. The end result is high purity PET flakes, sorted by color and ready to be used by the plastics manufacturing companies.

The stages of recycling process a scheme of technological process it is presented below:

		
Pre-sorting of appliances	Decontamination removal ✓ of batteries ✓ accumulators ✓ capacitors ✓ grind	Recovered materials: ✓ ferrous metals ✓ non-ferrous metals ✓ plastic
	Magnetic and inductive separation	

The final results from PET are flakes like in Figure 7.2, from which a lot of things can be done: from clothing (PET and polyester) to carpets, shoes, suitcases, upholstery, fibers for sleeping bags or down jackets, headlights, bumpers, grilles and door panels in cars, or, of course, other PET packaging.

Figure 7.2. PET flakes

The changes also occurred due to the presence of plastic in the oceans. This plastic crisis should be an opportunity to promote bioplastics. Bioplastics will not solve all plastic problems, but they will change the mindset and significantly reduce the environmental impact compared to traditional plastics. Plastic waste in the oceans is related to end-of-life challenges.

The added value of bioplastic:

- reduced CO_2 footprint,
- performant materials,
- a sustainable alternative to traditional plastics,
- the use of renewable resources as feedstock,
- valorization of waste streams,
- new applications for research and innovations.

The amount of garbage created is constantly increasing as economic growth means people buy more products and ultimately create more waste.

Population growth means there are more people on the planet, which will create waste. New packaging and technological products are being developed, and many of these products contain non-biodegradable materials.

The new added value of bioplastics it is present in Figure 7.3. Recycling is important both for the natural environment and for us. Humanity needs to act fast because the amount of waste they create is increasing all the time.

Nothing is lost, everything is transformed!
Green Plast Solutions

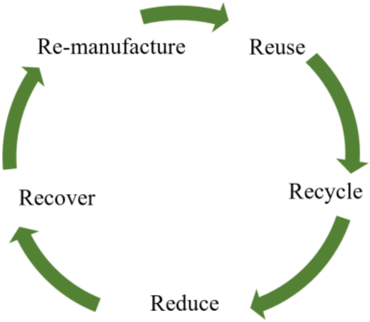


Figure 7.3. The new 5R's in plastic waste management

Another category of plastic products that are recycled is WEEE (Waste Electrical and Electronic Equipment). They are made up of materials that degrade over thousands of years, including toxic substances, and their mismanagement creates risks for health and the environment. This is precisely why modern and safe recycling services for all electrical or electronic equipment, batteries, cables, or components in the automotive industry are very important.

The recycling of WEEE is carried out through a simple process: electrical and electronic equipment contains hazardous substances, but also iron, aluminum, copper. And when properly recycled, valuable materials are reused as secondary raw materials and pollutants are removed in a controlled manner.

Examples of WEEE products - Coffee filters, IT equipment, toasters, vacuum cleaners or washing machines are converted into plastic fractions, ferrous and non-ferrous metals, glass, cables, and integrated circuit boards in one plant.

In Figure 7.4, the arrow triangle symbol seen on plastic containers and products does not necessarily mean that they are recyclable, it is the number represented within the symbol (1 to 7) that is important.

Figure 7.4. Plastic packaging codes

The purpose of these numbers is to help identify the type of plastic used to make the product, given that not all types of plastic are reusable or recyclable. Understanding the 7 codes makes the recycling process easier, as each of us knows which products are recyclable and which are not.

Now that it is known that there are different types of plastic and that some are more environmentally friendly than others, it is now possible to consciously choose small amounts and especially recyclable plastics.

Polyethylene terephthalate ***(PET)***

PET is one of the most widely used types of plastic. PET plastic products must be recycled, but not reused.

It's found in most water cans, but also in some packaging.
It is intended for single use, as repeated use increases the risk of releasing harmful substances, sometimes even carcinogens.
This type of plastic is difficult to disinfect, requiring dangerous chemicals to do so.
PET is a type of recyclable plastic, in the process the plastic is crushed and then shredded into small flakes that are then reprocessed to create other products.

High density polyethylene ***(HDPE)***

HDPE is a rigid type of plastic. HDPE products are reusable and recyclable.

HDPE is used in detergent bottles, toys and some bags, is the most commonly recycled type of plastic and is considered one of the least hazardous forms of plastic.
This type of plastic is durable and is not affected by direct exposure to the sun, so it is used to produce picnic tables, garbage containers, benches and other products that require durability.

Polyvinyl chloride ***(PVC)***

PVC is a type of soft and flexible plastic PVC products are not recyclable, and many of them are not even reusable

PVC it's used for food packaging, toys for children and pets, computer cables and other products.
This type of plastic is also called "poisonous plastic" because it contains numerous toxins that it releases during its entire life cycle.

Low Density Polyethylene ***(LDPE)***

LDPE products are reusable, but not recyclable.
LDPE products recycle are not very resistant.

LDPE is a type of plastic often found in heat-insulating packaging, dry cleaners' garment bags, shopping bags, and some clothes and furniture.
This type of plastic is considered less toxic than others, but it is not normally recycled.

Polypropylen ***(PP)***

PP is a type of hard and light plastic that has excellent heat resistance qualities.

It is used for packaging food (to keep it fresh), for making can lids, margarine and yogurt containers and straws.
PP products are considered safe for reuse, but their recycling is carried out only under certain conditions.

Polystyrene ***(PS)***

PS is a cheap, lightweight plastic.
PS products should be avoided where possible, their recycling being quite cumbersome.

Plastic with a wide variety of uses: from disposable cups and cutlery and egg cartons to construction materials.
Products from this material can release, especially as a result of their heating, carcinogenic substances.

7.5.Benefits of Biodegradable plastics

Graţiela Dana Boca

The benefit of using biodegradable plastic materials or bioplastics consists in the fact that they are made from natural plant-based raw materials that allow a natural decomposition process. This process occurs when bacteria and fungi present in the environment naturally metabolize plastics. The process of decomposing plastic waste continues by turning it into compost after a certain period.

Biodegradable plastics are used in many areas shopping bags, the medical department bottles, tea bags, jars, air pillow, pens, pencils sharpeners, etc.

Below are four reasons why biodegradable plastics benefit the environment and help conserve natural resources:

- save non-renewable energy sources,
- reduces carbon emission,
- consumes less energy,
- provides an eco-friendly solution.

Biodegradable plastic is of great importance because it helps the environment by eliminating waste, helping to create a greener and more sustainable future for our planet.

List of advantages of biodegradable plastics:

- carbon emission reduction,
- consumes less energy,
- less landfill area needed,
- recyclable.

The advantages of biodegradable plastics for the environment are:

- biodegradable plastics are easy to recycle,
- recycling helps to reduce landfill problems,
- the manufacture of bioplastics does not require the process of finding,
- compostability,
- reducing carbon dioxide levels,
- reduction of greenhouse gas emissions,
- reduced oil consumption.

Throwing away traditional plastics can also mean releasing methane, toxic chemicals, and other types of pollutants into the environment. These substances, while decomposing, are potentially dangerous as they can easily harm marine and terrestrial ecosystems as well as human health in general.

Switching to biodegradable plastic products means reducing the release of these lethal products into the environment and creating a better and healthier future for future generations.

Biodegradable plastic products are broken down by naturally occurring bacteria.

When buried in soil, soil bacteria begin to break it down, this decomposition process is natural, so the amount of fossil fuel or energy consumed in the process is nil and therefore it is also cost-effective.

Biodegradable plastic products can be made to break down under specific conditions when their decomposition is easier and less harmful but under specific conditions.

Nicholson and Leighton in 1942 and later Freinkel (2011) study the advantages of bags and now the new biodegradable plastic bags which are on high quality standards. Also, there are multiple benefits to choosing biodegradable bags, here are some reasons why you should choose biodegradable packaging products in our daily life:

- reduction in carbon emissions,
- waste reduction,
- repurposing and recycling,
- reduced pollution,
- non-toxic.

7.6.Disadvantages of Biodegradable Plastics

Graţiela Dana Boca

The disadvantages of biodegradable plastics are listed below:

- need for composters,
- engineering issues,
- risk of contamination,
- biodegradable plastics are made from plants,
- biodegradable plastics may contain metals,
- need for costly.

A benefit of biodegradable bags is the positive effect it has on consumers, through brands known to consumers.

Thus, successful companies have a new role not only as a producer of branded products but also as an educator of their customers, to lay the foundations of a green culture.

A significant example is Coca-Cola who already use bio plastic products, by promoting ecological options it has a positive impact on the brand along with protecting the environment.

http://pakbec.blogspot.com/2010/10/plastic-from-plants-is-it-environmental.html

7.7.Sustainable Environment

Graţiela Dana Boca

A product or material is sustainable if it is also sustainable from an ecological, economic, and social point of view.

There are three pillars on which sustainability can be realized and bring a positive contribution for new biomaterial to be sustainable: environmentally, economically, socially sustainable. From Figure 7.5, three components of sustainability can be identified.

Plastics make a huge contribution to environmental sustainability through their energy saving potential and intrinsic recycling and energy recovery options. From an economic point of view, plastics are an important part of the economy. Socially, the plastics industry is a major and inclusive employer with a focus on training and education.

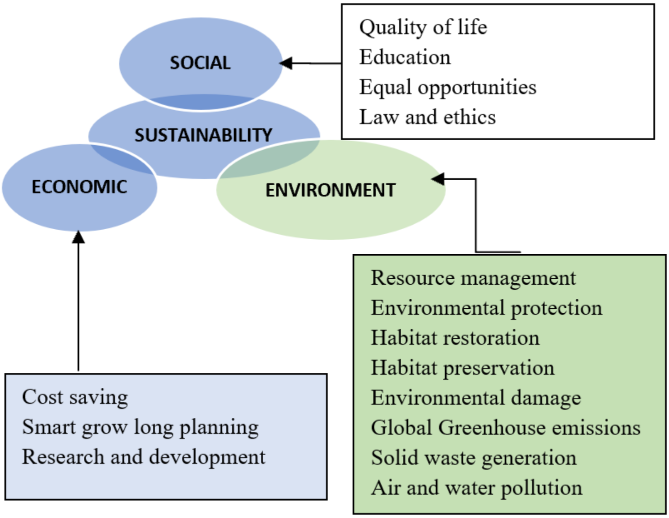


Figure 7.5. Relation between sustainability components

Plastic materials have a very good ecological profile and consequently, plastic can be seen as a “borrow” of oil.

7.7.1. Environmental sustainability

Environmental sustainability is an important component and environmental degradation and extreme changes in the natural environment are part of the challenges of sustainable development. Sustainable development requires improving human well-being, but the consequences of climate change and the growing demand for energy and resources make this goal more difficult.

Plastics have a very good environmental profile. When plastics have completed their use phase, they can be recycled but it is not economic or environmentally beneficial the calorific value of the plastic can be recovered through energy from waste incineration.

The specific fields where plastic has an important role are:

- packaging,
- construction,
- transport,
- waste management: plastics recycling and energy from waste.

Waste management represents the following stages: collection, processing, treatment, and recycling of waste. The connection between circular economy and plastic waste it is presented in Figure 7.6. Within the Waste Management process, the storage, transport, treatment, and disposal of waste must also be identified, monitoring, overseeing, and regulating development, processing, transit, treatment, and disposal for the better health of our environment.

Waste control or disposal is the totality of behaviors and actions required to handle waste from its inception to final disposal. This includes, but is not limited to, the storage, transport, and management and recycling of waste along with control and enforcement.

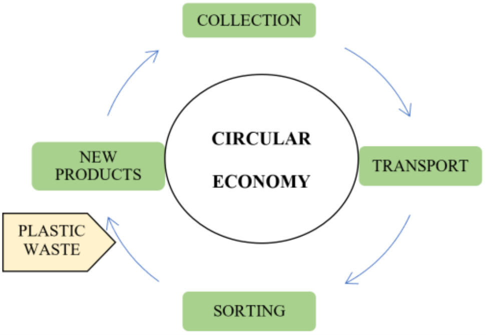


Figure 7.6. The connection between circular economy and plastic waste

In Figure 7.7 different new types of recycling used in waste plastic management can be identified. Thanks to recycling, not only the environment and resources are protected for future generations, but also energy consumption and greenhouse gas emissions are reduced.

It can be seen that the methods differ depending on the type of material to be recycled. Here is biological method, mechanical, thermochemical and transformation method. It can be identified that the impact of the recycling process can bring benefits such as conversion to fuels and chemicals, incineration, and recovery of heat from biogas.

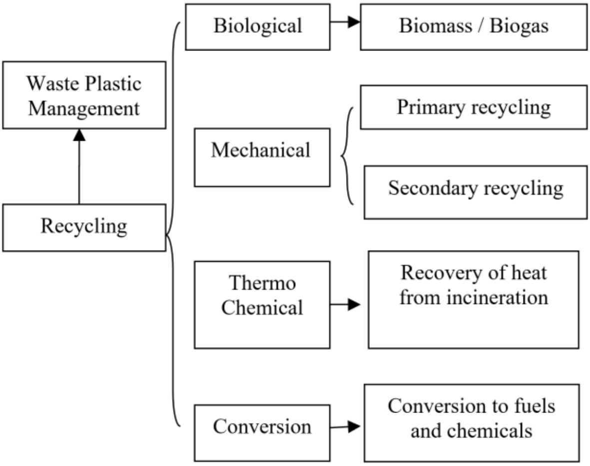


Figure 7.7. Types of recycling used in waste plastic management. (Adapted after Idumah and Nwuzor (2019))

7.7.2. Economic sustainability

Plastics take a major contribution to economy and a healthy manufacturing sector is vital to a sustainable economy. Plastics also have a role to play at a micro-economic level:

- constantly developed and improved, promoting innovation,
- low maintenance, no painting required,
- reduced energy required for heating when using plastic insulation,
- plastic products are very cost effective for the ability to make individual molded components in complex shapes,
- plastic products also offer lifetime cost savings.

Plastic pollution is a threat to the environment and human health. The solution to reuse and recycle plastic waste through various sustainable technologies can transform plastic into valuable products.

7.7.3. Social sustainability

The social component of sustainability refers to the rights and well-being of all people. Social sustainability is an ongoing, long-term mission to ensure that social conditions and outcomes are optimized for generations.

Social sustainability is:

- safety,
- health,
- personal relationship,
- equality,
- environment and services,
- inclusion,
- industrial empowerment.

7.8. Circular Economy

Graţiela Dana Boca

The circular economy is a model of production and consumption that involves sharing, renting, reusing, repairing, refurbishing, and recycling existing materials and products for as long as possible. Thus, the life cycle of the products is extended (afrik21.africa/en/africa-the-afdbs-commitment-to-the-transition-to-the-circular-economy/).

In practice, it involves minimizing waste. When a product reaches the end of its life cycle, the materials from which it is made are kept in the economy as much as possible. They can be used in production again and again, creating even more added value.

It is an approach that differs radically from the traditional, linear economic model, based on the use-produce-consume-throw principle. This traditional model relies on large quantities of cheap and easily accessible materials and energy.

This model also includes programmed obsolescence, with products designed to have a limited lifespan to encourage consumers to buy again. The European Parliament called for measures to combat this practice.

The circular economy can have the following definition: it represents an ideal model of production and consumption aimed at the manufacture, use and reuse of all recyclable raw materials, to put them back on the market and help them have as long a life as possible. Thus, production and reuse become the keywords of the circular economy.

Circular economy means sustainability and is an important aspect of sustainability. In this way, people's existing solutions are developed without consuming natural resources. The circular economy focuses a lot on the future of the planet because raw material resources are becoming increasingly scarce.

7.8.1. The benefits of the circular economy

Numerous studies show that the global population is constantly increasing, and this means an increasing demand for raw materials. However, the supply of raw materials is increasingly limited. For example, many of the European Union countries produce wood, paper, plastic, glass, steel, aluminum, etc. It becomes necessary to keep the other one to buy materials such as.

First, their extraction and use have a major, extremely negative impact on the environment, but not only that. They increase CO_2 emissions and energy consumption. With their much more efficient and intelligent use, emissions will be reduced considerably.

Also, some of the benefits are:

- Pressure on the environment is considerably reduced,
- The supply of raw materials will no longer represent a problem,
- Deforestation will be increasingly rare or eradicated,
- Businesses will create new jobs,
- Innovation is stimulated,
- Increases competitiveness,
- Economic growth will begin,
- Customers and consumers will enjoy much higher quality products,
- Innovative and sustainable products,
- The company will be able to save money in the long term,
- The quality of life is increased.

7.8.2. Circular economy – concept and implementation

For the circular economy to be implemented, certain objectives must be pursued. For example, the linear model of make, use and store prevailed in the European Union and, including in Romania, once the industrial revolution began. That's why it is aimed to distance ourselves from these habits that are so well rooted in the population.

Now is the time when society must eliminate the "take, produce, use, throw away" mentality. In its place comes the concept of circular economy, which is based on extending the life cycle of all products on the market, so that the raw materials used become less and less, and waste is as small as possible.

Thus, a circle is created in which the stages of this concept are continuously repeated: raw materials, design, production or manufacture, distribution, consumption, use, reuse or repair, collection (where residual waste comes out of this cycle) and recycling what can be reused, so that quality raw materials are reintroduced at the beginning of this process.

The notion of a circular economy must be understood by society in the sense that it creates values, knowledge and a behavior that develops and gives rise to positive attitudes regarding the environment and the importance of waste recycling. Thus, to reach the threshold of zero waste, an education is needed in this sense, which ensures initiatives for the management of raw materials, energy conservation, climate change and many other problems that all the world’s population is facing at this moment.

So, even by adopting measures of this kind, a business can help the population become aware of the importance of the circular economy and benefit from a sustainable image, which many users are starting to look for.

7.8.3. The principles of the circular economy

The circular economy is based on the principle of recycling, reusing, or repairing raw materials and waste so that they can be used again and again. This concept is promoted by the European Parliament and imposed on member countries.

The circular economy is recognized for its 5 pillars:

- ***sustainability of resources*** – renewable, recyclable, biodegradable materials or any resource that reduces the amount of waste is used,
- ***life extension*** – new methods are developed for the design and manufacture of products, so that they have as long a life span as possible. Resources that would normally have been lost through material waste are repurposed to aid in repair, remediation, or remarketing,
- ***product equals service*** – the business that made the product must offer not only the object or service itself, but also additional related benefits, such as assistance or trainings,
- ***sharing platforms*** – with their help users and customers are informed about how to benefit as much as possible

from a product, how to use resources intelligently or how to save with the help of recycling,
- ***end of life*** – creating production systems that use goods considered waste as resources for new products.

The transition from the linear to the circular model can represent an opportunity for a business to develop a sustainable innovation. Thus, they can focus on differentiating their products and services through modularity, longevity, repair, and recycling. Also, after a user deems a product good to throw away, the company from which it was purchased can take it back, with the goal of repairing and reusing it.

Economy for plastic actions are:

- ***Eliminate*** - Eliminate all problematic and unnecessary plastic items,
- ***Innovate*** - Innovate methods and technologies for plastics using the 3R’s,
- ***Circulate*** - Circulate all the plastic by reuse in the economy and not harming the environment.

The new trend towards the throw away culture of society is growing, but at the same time recycling and waste management are not only necessary, but also desired by the public. This phenomenon requires a shift from waste management to materials management.

Linear economy follows, take-make-dispose steps. Raw materials are collected, then transformed into products that are used until they are finally discarded as waste.

Value is created in this economic system by producing and selling as many products as possible.

Figure 7.8 includes a model for the plastic linear economy, where the stages from raw materials to waste plastic can be seen, and at each stage, economic impact factors, health problems and finally environmental impacts, reasons for action are included.

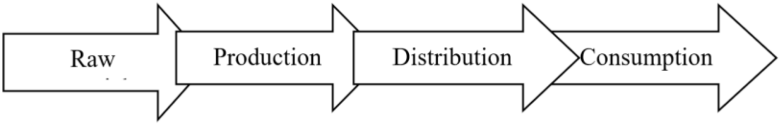


Figure 7.8. Linear economy model for plastic

The challenges related to the transition to a circular economy are mainly due to the systemic barriers present in the current linear economy:

i) Institutional barriers

Absence of fair competition conditions: The current economic system is oriented towards the demand of the linear economy.

In addition, new circular business models (e.g. the sharing economy) may conflict with current norms, regulations and agreements on working conditions.

Focus on the traditional value chain: To close the loops, new alliances are needed outside the traditional value chains.

Short-term outlook: Many companies pursue short-term perspectives.

ii) Social barriers

Low awareness. Appreciation for property: Property is often closely related to status and current tastes. Functionality may be subject to full product availability. A new product may have preference over a used product.

Consumer barriers: Understanding and evaluating what the concept represents. To reach the mass market, a product certification or labeling system may be required. Key barriers include the lack of standardization of methodologies applied across countries, the cost of assessing resource consumption for individual firms, and the absence of a widely recognized independent organization that grants resource efficiency or circular economy certification.

iii) Economical barriers

iv) Energy and material barriers

The circular economy will help reduce waste and keep materials in the economy. Landfills and incinerators, and the expansion of waste solutions remain a challenge, as the linear model of production, consumption and disposal must be adapted to today’s new requirements. The circular economy follows the 3R’s approach: reduce, reuse, and recycle (Figure 7.9).

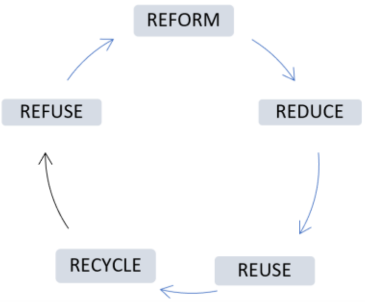


Figure 7.9. The 5R's pillar of plastic waste management

In the because of the dynamic characteristic of quality, innovation and technological needs another R's was taken in consideration respectively resource usage to be minimized (reduced). Reuse of products and parts is maximized (reuse). And last but not least, the raw materials are reused (recycled) to a high standard.

The concept offers a circular process of inputs and outputs to ensure materials and resources remain in the production and consumption process.

It encompasses three principles: **i)** design out toxins, waste, and pollution, **ii)** keep products and materials in use, **iii)** regenerate natural systems.

The circular economy concept offers an alternative to the current linear: take, make, dispose model of the economy, and aims to keep resources in use as long as possible, to extract maximum value from them and to recover and regenerate products and end-of-life materials. In Figure 7.10, it is possible to see the following stages for the plastic circular economy model:

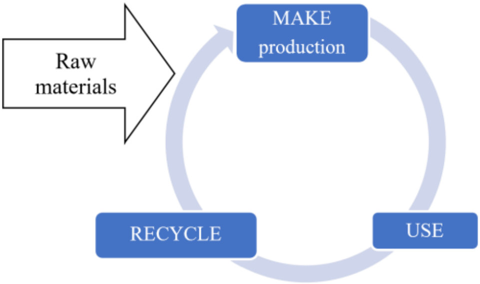
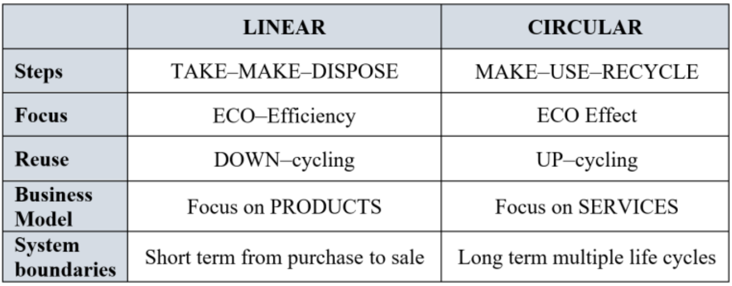


Figure 7.10. A model for plastic circular economy

The circular plastic economy is a model that promotes the reuse of plastic products, generates value from waste and recovers plastic. The circular economy for plastic is characterized by the following key elements:

- eliminating plastic packaging by creating new models,
- reduction of single-use packaging,
- plastic packaging is reused, recycled, or composted in practice,
- the use of plastic does not require consumption of finite resources,
- plastic packaging does not contain dangerous chemicals.

The differences between the two business models linear and circular economy are the following like in the table below:



	LINEAR	CIRCULAR
Steps	TAKE–MAKE–DISPOSE	MAKE–USE–RECYCLE
Focus	ECO–Efficiency	ECO Effect
Reuse	DOWN–cycling	UP–cycling
Business Model	Focus on PRODUCTS	Focus on SERVICES
System boundaries	Short term from purchase to sale	Long term multiple life cycles

The circular economy for plastics considers every stage of a product’s life cycle and the actions specific to the circular economy for plastic are:

- removal of plastic objects,
- innovation of plastic materials and their reuse, recycling, or compost ability,
- circulation of plastic articles in the economy and outside the environment.

Circular economy solutions for plastics should focus on the elimination of single-use plastics and the efficient management of long-life plastics such as those used in vehicles and construction.

Circular economy solutions for plastics include:

- using plastic waste as a resource,
- designing non-toxic degradable alternatives to single-use plastic,
- encouraging recycling,
- adoption of new and sustainable business models,
- development of information platforms to help circular solutions.

The conceptualization and practice of circular economy has so far largely been undertaken by academics, policy makers, businesses, and foundations, while the implementation remains inadequate. Where waste management is not developed and implemented, it is often the poorest people that bear the greatest cost of plastic pollution and environmental degradation.

Where government and business have not taken the necessary actions, local communities and grassroots organizations have often initiated their own small-scale circular economy initiatives to reduce the impacts of plastic litter on their environment and to relieve the pressure on local ecosystems and services.

7.9.Greenization Factor as a Sustainability

Graţiela Dana Boca

Greenization is the process of coordinated development and growth of the systems of the economy, society, and resources and the environment (Liu et al., 2016).

In this process, the efforts towards greening and the targets of these systems, whose effects are green growth, green welfare, and green wealth, are seen in Figure 7.11.

As a conclusion, it can be said that there is a balance of quality, respectively between the efforts made and the effects obtained.

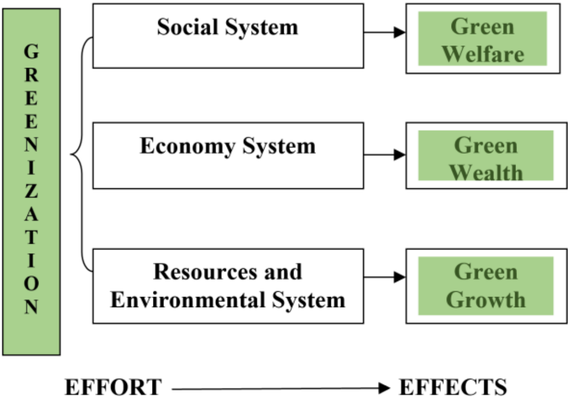


Figure 7.11. Quality balance of greenization process
(Adapted from (Liu et al., 2016))

7.9.1.Short history of phenomenon of greenization

To understand the phenomenon of greenization, Bin et al. and Wang et al. presented a short brief review of ecological industrial development and ecological development (Bin et al., 2010; Wang et al., 2020).

The phenomenon appeared in 1962, when American biologist Rachel Carson published The Silent Spring, in which she showed that the use of chemicals and fertilizers harms human beings and the environment. That is why they proposed to people to reflect on the environmental damage caused by economic and technological development.

Bin and Xuanya, and later Wang et al., mention then later, the Club of Rome, a private academic organization, published a research report titled The Limits to Growth, which warned the world to pay close attention to the relation between human and environmental and resource consumption (Bin and Xuanya, 2016; Wang et al., 2020).

Over time, the relationship between economic growth and resources, environment, and sustainability, has been carefully studied so that new concepts such as green economy, green growth and green development have appeared and the relationship between economy and ecology has been studied. These concepts of green economy and green development have been emphasized and ecological industrial policies have also been harmonized for each country and economy.

The United Nations Industrial Development Organization (UNIDO) has established an indicator system for industry greenization development such as natural resource, environment, and greenhouse gases (GHG) emission (Hall et al., 2006).

Chuanzhi and Haochang in their research establish a correlation between industrial concentration and environmental pollution as an indicator system for green economy launched by United Nations Environment Programme (UNEP) which measures the development of green economy on the three fronts of (Chuanzhi and Haochang, 2017):

- economic transition,
- resource efficiency,
- social benefits.

Chunanzhi and Haochang (2017) study the correlation between ecological footprint and economic and industrial development under the set-up of The Organization for Economic Co-operation and Development (OECD) based Wang et al. (2020) research on low-carbon economy evaluation system, which is comprised of such aspects as human activities, ecological balance, environmental quality, and natural resources.

In time industrial greening needs studies from the perspective of indicator system or input–output ratio. Jänicke proposed green growth and based on industrial data of countries like Germany, Japan, and China, proposed that it is necessary to improve the resource productivity, such as through better energy-saving technologies and economize the environment and resources to achieve sustainable growth a direct relation between economic development and ecological footprint like Jianxing et al. suggest (Jianxing et al., 2005; Jänicke, 2012).

Industrial greening has become a priority in the context of the global market economy, thus ecological development has become the main priority, especially of resource conservation, environmental protection, and sustainable growth.

Maochu (2015) and Wang et al. (2020), believed that environmental industry and industrial greening are limited adaptation on the industrial level to ecological biocapacity. Jingsheng (2009) and later Maochu (2015) proposed an eco-environmental consumption quota system to measure industrial greening and promoted environmental protection industry as a way to boost industrial greening.

Kroll (2001), Li (2018), Liyang et al. (2013) and Maochu (2015) evaluate and put in evidence also the mistakes in greening industrial development.

7.9.2.What are green plastics?

Green plastics or bioplastics are plastic materials that are either biodegradable, made partially or entirely from biological materials or both above.

The use of biodegradable plastic is already popular because it can reduce greenhouse gas emissions, dependence on fossil fuels and shrink landfills.

Removing plastic from the circuit and replacing it with the new bio-degradable plastic is at the beginning of the road, but in the future, it shows the potential for incredible growth. The most used bioplastics are:

- Polyethylene terephthalat,
- Polyethylene (PE) and Polypropylene (PP),
- Polylactic acid (PLA).

There are numerous other green plastics like Polyhydroxy Alkanoates (PHAs), Cellulose Acetate (CA), and Polyamide (PA) that are being developed and implemented in various industries (https://www.plastivision.org/blog/what-are-green-plastics-their-environmental-benefits/).

7.9.3.What are green plastics and their environmental benefits?

Awareness and concern about environmental degradation is growing rapidly. As a result, a growing number of businesses and innovators are focusing on environmentally sustainable alternatives. One such alternative that has emerged is called “Green Plastic”. Figure 7.12 shows the connection and its impact on the environment.

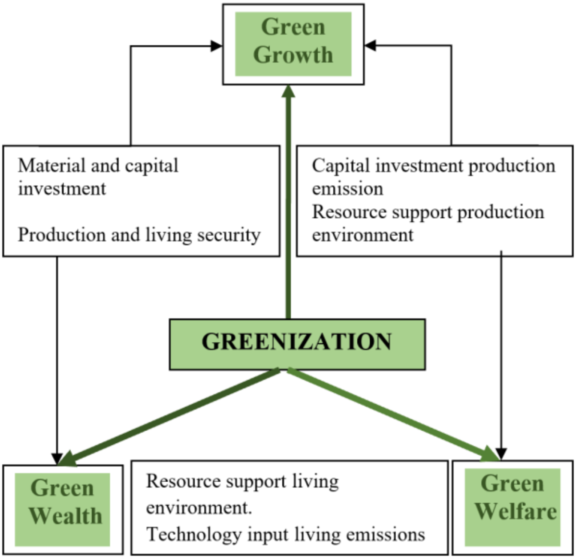


Figure 7.12. The impact of greenization

Plastics can be found everywhere around us, most of these plastics (hydrocarbon plastics) are traditionally made from nonrenewable oil-based products. Green plastics are biodegradable plastics made from plant-based polymers.

Benefits of Green Plastics:

- lower environmental impact green plastics are better for the environment,
- green plastics help in reducing the waste that occupies landfills,
- customer appeal,
- time savings.

The connection between the three elements of greenization are:

Green Growth	Material and capital investment Production and living security	**Green Wealth**
Green Growth	Capital investment production emission Resource support production environment	**Green Wealfare**
Green Wealth	Resource support living environment Technology input living emissions	**Green Wealfare**

7.10. Opportunities and Human Resources

Graţiela Dana Boca

Another benefit of the circular economy is innovation. Businesses create new jobs, which mean that market competitiveness will increase considerably in all fields of work. This means that any business, whether it is a start-up or a multinational company, will have to reinvent itself, offer new benefits to its customers and find new ways to innovate their products and packaging. Thus, all this represents a major economic boost for any country that adopts the circular economy.

The circular economy considers every stage of a product's before and after it reaches the customer. Stopping plastic pollution also offers economic, social and climate benefits and by 2040, a circular economy has the potential to:

- reduce the annual volume of plastics,
- reduce greenhouse gas emissions by 25%,
- create additional jobs.

The bio plastics industry in Europe by 2030, together with a legislative framework appropriate to the markets, will be able to offer many jobs. The bio plastics industry could enable the development of rural areas in Europe by presenting new opportunities for the agricultural sector and for re-industrialization and employment growth in Europe. Feasibility studies showed that bioplastics could technically substitute about 85 percent of all conventional plastics even though this is not a realistic short- or mid-term development, it illustrates that bioplastics will be a significant part of the overall plastics market in the future.

7.11. Market drivers and development

Graţiela Dana Boca

Bio plastics offer additional advantages, such as a reduced carbon footprint or better waste management. Waste can be an opportunity to create jobs and reduce costs. The demand for new jobs on the bio plastics market is characterized by a dynamic growth rate and strong diversification.

The wide range of uses of bio plastic from beverage bottles in the packaging segment to keyboards in the consumer electronics segment and interior parts in the automotive sector also required new specialized employees.

The introduction of different bioplastic materials with the new products will raise the level of awareness and information significantly. Increasing volumes of bioplastics on the market, higher production costs will soon adapt to prices paid for conventional materials.

The bioplastics industry in Europe by 2030 can bring a number of new jobs with the help of an appropriate legislative framework and the robust implementation of unifying market conditions. Also, the new orientation will be an engine for the market and its development.

Ensuring the replacement of plastic with bioplastic for almost every conventional plastic material and the corresponding application will also attract the creation of new jobs. Applications for the new bio plastic include a wide range of uses, from soft drink bottles in the segment, to packaging or in the electronics field to keyboards or parts in the automotive sector.

One effect of the transition to the circular economy and employment will be employment that will increase as countries move to a circular economy. These jobs will be created by increasing:

- expenses and price reduction,
- labor requirements for recycling and quality repair works,
- personnel from the logistics sector for local processing of products,

- innovative elements and services in new business models,
- increasing incentives for innovation.

Type of Operation	Computer reuse Textile reclamation Durable reuse Wooden pallet repair Recycling based manufacture Paper mills Glass product manufacture Plastic product manufacture Conventional materials recovery facilities Composting

The circular economy calls for innovative solutions based on a new way of thinking. Reflecting on circular value chains and aiming to optimize the entire system of an organization, resulting in new perspectives and an interdisciplinary collaboration between designers, manufacturers, and recyclers, as well as sustainable innovators. In waste management reuse operations mention the new jobs opportunities. A circular economy can create jobs Figure 7.13.

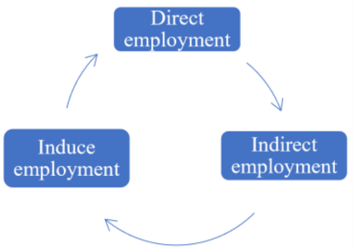


Figure 7.13. New jobs in waste plastic

Also, there are some benefits from recycling which can create job opportunities following section:

- product and packaging manufacturing,
- collecting and sorting,
- mechanical recycling,
- advance chemical recycling,
- retailer collection,
- landfill,
- energy recovery.
- recycling of packaging and paper products from households.

Highlights

- Linear economy follows, take-make-dispose steps.
- The notion of a circular economy must be understood by society in the sense that it creates values, knowledge and a behavior that develops and gives rise to positive attitudes regarding the environment and the importance of waste recycling.
- The Waste Management process goes through several stages: storage, transport, treatment, and disposal of waste; monitoring, overseeing, and regulating development, processing, transit, treatment, and disposal for the better health of our environment.
- Green plastics or bioplastics are plastic materials that are either biodegradable, made partially or entirely from biological materials or both above.

- Greenization is the process of coordinated development and growth of the systems of the economy, society, and resources and the environment.

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CHAPTER 8: PAST, CURRENT AND FUTURE OF BIODEGRADABLE PLASTICS: INNOVATIVE APPLICATIONS

Massimo Bersani

8.1.Brief History of Plastic and Bioplastic

Massimo Bersani

Plastic has a rich history dating back to the mid-19th century when scientists began to experiment with various chemicals and natural materials in an effort to create a substitute for materials such as ivory and tortoise shell.

However, it was not until the early 20th century that plastic became widely used in industry and consumer products. The invention of Bakelite, the first synthetic plastic, by Belgian chemist Leo Baekeland in 1907 was a significant breakthrough in the development of plastics. Bakelite was a thermosetting plastic that could be molded into any shape and was highly durable, making it ideal for use in electrical and automotive industries.

During World War II, plastic production increased dramatically as it was used in a variety of military applications, including aircraft parts, parachutes, and insulation. After the war, the demand for plastic continued to grow as it became a popular material for consumer products such as toys, household items, and packaging.

In the 1950s and 1960s, the petrochemical industry developed new types of plastics, such as polyethylene and polypropylene, which were cheaper and easier to produce than earlier plastics. These new plastics were used in a wide range of applications, from food packaging to construction materials.

Plastic's popularity continued to grow throughout the latter half of the 20th century, and by the 1990s, it had become one of the most ubiquitous materials in the world. However, concerns about plastic pollution began to emerge as plastic waste accumulated in oceans and landfills, leading to efforts to reduce plastic consumption and increase recycling.

Following a list of plastic products are reported.

- Bakelite (1907) - Bakelite was the first synthetic plastic invented by Belgian chemist Leo Baekeland in 1907. It was a thermosetting plastic that could be molded into any shape and was highly durable, making it ideal for use in electrical and automotive industries.

- The commercialization of PolyVinylChloride (PVC) in 1927 is the direct result of research work that was conducted by Waldo Semon, a chemist working at the B.F. Goodrich Rubber Company. PVC is one of the most widely used thermoplastics in use today, particularly in the building and home construction industries where it is used for siding, window profiles and pipe.

- Nylon (1935) - Nylon was invented by American chemist Wallace Carothers in 1935. It is a strong, lightweight, and durable material that revolutionized the textile industry, making it possible to create synthetic fabrics that were more affordable and versatile than natural fibers.
- Tupperware (1946) - Tupperware was invented by Earl Tupper in 1946. It was made from polyethylene, a plastic that was highly durable and resistant to breakage. Tupperware was marketed as a new way to store food, and it quickly became a popular household item.
- Plastic bottles (1947) - Plastic bottles were first introduced in 1947 by the American company Owens-Illinois. They were initially used for soft drinks, but their popularity quickly grew, and they became a ubiquitous packaging material for beverages and other products.
- Disposable diapers (1949) - Disposable diapers were first introduced in 1949 by Swedish engineer Paul G. Karlsson. They were made from a combination of plastic and paper and were designed to be more convenient and hygienic than cloth diapers.
- LEGO bricks (1958) - LEGO bricks were first introduced in 1958 by the Danish company LEGO. They were made from acrylonitrile butadiene styrene (ABS), a plastic that is strong, durable, and easy to

mold into various shapes. LEGO bricks quickly became a popular toy around the world.

- Plastic shopping bags (1960s) - Plastic shopping bags were first introduced in the 1960s and quickly became a ubiquitous item in retail stores around the world. They were cheap, lightweight, and durable, making them an ideal packaging material.
- Kevlar was first developed by the American company DuPont in the 1965. Its main feature is the great mechanical resistance to traction combined with heat resistance. It is used as technical clothing and body armor, as well as structure in vehicles. Cost 2 orders of magnitude compared to PET.
- PET bottles (1973) - PET (polyethylene terephthalate) bottles were first introduced in 1973 by the American company DuPont. They are lightweight, durable, and resistant to breakage, making them a popular packaging material for beverages and other products.
- Computer keyboards (1980s) - Computer keyboards were first made from plastic in the 1980s. They were made from a combination of ABS and polycarbonate, two plastics that are strong, durable, and easy to mold into various shapes. First were made in wood.
- Smartphone cases (2000s) - Smartphone cases were first introduced in the 2000s and quickly became a popular accessory for mobile devices. They are made from a variety of plastics, including polycarbonate,

polyurethane, and silicone, and are designed to protect the phone from damage.

- Many vehicles incorporate a large amount of plastic. For example, plastic is used in various components of the Boeing 747, including the interior components, such as seat backs, overhead bins, and wall panels and in various structural components, such as wing flaps and fairings.

In Figure 8.1 a timeline of plastic history is reported:

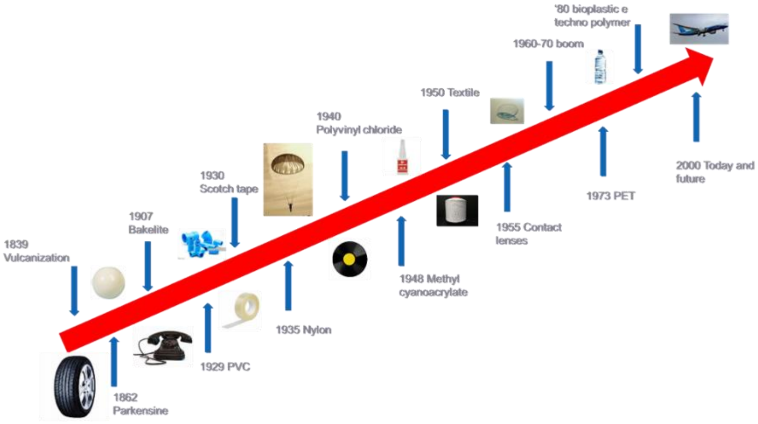

Figure 8.1. Plastic product timeline

Today, plastic is still widely used in a variety of industries and products, but there is increasing awareness of its impact on the environment. Efforts to develop more sustainable and biodegradable plastics are ongoing, and many countries have implemented regulations and bans on certain types of single-use plastics to reduce their environmental impact.

First biodegradable plastics were developed in the 1970s, using starch and other plant-based materials. In the decades since, bioplastics have become increasingly popular, as environmental concerns and sustainability have become more pressing issues.

These bioplastics were designed to be biodegradable and compostable, meaning they could break down into natural materials over time, reducing waste and environmental impact.

Over the past few decades, bioplastics and biodegradable plastics have become increasingly popular as environmental concerns and sustainability have become more pressing issues. Today, they are used in a wide range of applications, from disposable products such as cutlery and packaging to more durable products such as electronics and automotive components.

Today, bioplastics are used in a wide range of applications, from packaging and disposable items to more durable products such as electronics and automotive components.

Some of the main products obtained by bioplastics include:

- ***Packaging materials:*** Bioplastics are commonly used to produce packaging materials such as bags, films, and containers. These materials are often biodegradable and compostable, which reduces waste and environmental impact. The first county in the world that use bag in bioplastic was the Bangladesh in 2002 in Italy bioplastic bags become mandatory in 2018 after several delays and a long negotiation with European Commission.

- ***Disposable cutlery and food service items:*** Bioplastics are also used to produce disposable cutlery and food service items, such as plates, cups, and utensils. These products are often made from polylactic acid (PLA), which is a biodegradable and compostable material.
- ***Textiles:*** Bioplastics can also be used to produce textiles, such as clothing, bags, and accessories. These materials are often made from bio-based polymers such as bio-polyesters or polylactic acid (PLA).
- ***Electronics and automotive components:*** Bioplastics can be used to produce durable components for electronic devices and automobiles. For example, bioplastics can be used to produce circuit boards, casings, and other components that require high strength and durability.

Despite their benefits, bioplastics and biodegradable plastics still face challenges, such as the cost of production and the availability of suitable disposal and recycling facilities. However, ongoing research and development continue to improve the properties and performance of these materials, making them an increasingly viable alternative to traditional plastics.

8.2.Plastic Impact on Society and Culture

Massimo Bersani

"*I just want to say one word to you. Just one word…. Plastics…. There's a great future in plastics.*"

"The Graduate", 1967 American movie direct by Mike Nichols, with Dustin Hoffman

Plastic is not only the reference material on which the second industrial revolution was based, just as steel was for the first industrial revolution. Plastic represents all our technologies. It has spawned an entire industrial ecosystem, a large-scale technological system, which can no longer be controlled or managed at will. We have created a self-generating system supported by needs and a collective ethic.

Plastics have also shaped a new concept of technological design and a specific relation between humans and materials. They have encouraged the dream of dematerialized and disposable artefacts (Gabrys et al., 2017).

Plastic has had a terrific impact on modern society, both positive and negative. On the positive side, plastic has made many products cheaper, lighter, and more durable, which has improved our quality of life in many ways. Plastic is used in everything from packaging to medical devices to electronic components, and its versatility has made it a key material in many industries.

Negative side is manly represented by Plastic waste a major environmental problem, with millions of tons of plastic ending up in landfills, oceans, and other ecosystems every year. Plastic takes hundreds of years to break down, and as it does, it releases harmful chemicals into the environment. Plastic waste also poses a threat to wildlife, which can ingest or become entangled in it.

Between the world war plastics did not only substitute material for existing object but they start to generate new concept a kind of artifacts and modify the relationship by human and objects.

Plastic created the conditions for global trade and consumerism, it can be considered the substrate of advanced capitalism (Dworkin, 2013).

The impact of plastic on capitalism is complex and structured in different level. It has been a boon to capitalism, allowing companies to produce goods more efficiently and profitably. The low cost of plastic has also enabled the growth of disposable consumer culture, where products are designed to be used once and then thrown away, contributing to a throwaway culture that is not sustainable.

Plastic is a symbol of the modern era's aspirations, embodying the promise of a flawless, hygienic, and abundant world. It reflects the ideal of purging the earth of filth, rot, and corruption. As asserted by Westermann, vinyl's malleability and synthetic origin epitomize what advanced technology in the modern age aimed to achieve:

liberation from the limitations imposed by nature on humanity. This also implies the elimination of scarcity, ushering in a world of boundless prosperity (Gabrys et al., 2017).

To have a wide and detailed vision of Plastic impact we suggest Jeffrey Meikle book “American Plastic: a cultural history” (Meikle, 1997).

Plastic has also penetrated our Pop culture. Iconic Hollywood movies report plastic:

“It’s a wonderful life” (1948) by Frank Capra

“Barbarella” (1968) by Roger Vadim with Jane Fonda

The previously cited “The Graduate”.

In the 60’s plastic impacted also in the high fashion. In fac in 1968 Paco Rabanne realized the first plastic dress (The Metropolitan Museum of Art).

Several Novel books are also based on plastics and its impact on society, below a personal choice is reported:

“Plastic Dreams” by Kisha Nicole Foster - This novel explores the impact of plastic pollution on the environment.

“The Garbage King” by Elizabeth Laird - A story of a street child in Ethiopia who makes a living by scavenging through trash, including discarded plastic waste.

“The Great Pacific Garbage Patch” by Jillian Morris and Duncan Brake - This novel is a fictionalized account of the impact of plastic pollution on marine life.

“The End of Mr. Y” by Scarlett Thomas - Where plastic turn into consciousness.

“Invisible Cities” by Italo Calvino - This novel is a collection of short stories that explores the relationship between cities and their inhabitants, including the proliferation of plastic waste.

“The Mutant 59: The Plastic Eater” by Kit Pedler and Gerry Davis. Science fiction story, where a new strain of bacteria that can digest plastic. The bacteria begin to consume all forms of plastic, including vital infrastructure like electrical wires and medical equipment. The book gives the vision of a world without plastic.

In conclusion, while plastics have brought many benefits to society and culture, their negative impacts on the environment, consumerism, labor practices, and public health cannot be ignored. As a global community, we must take responsibility for the consequences of our actions and work towards a more sustainable future. Bioplastics can have a positive impact on the future to reduce plastic waste and related pollution, mitigate the dependences for fossil fuel, improve innovation, address a consumer education.

Highlights

- Plastic has a rich history dating back to the mid-19th century when scientists began experimenting to create a substitute for materials like ivory and tortoise shell.
- Plastic became widely used in industry and consumer products in the early 20th century, with the invention of Bakelite, the first synthetic plastic, in 1907.

- During World War II, plastic production increased significantly for military applications.
- Plastic's popularity continued to grow after the war, becoming a common material in consumer products, toys, household items, and packaging.
- The petrochemical industry developed new types of plastics in the 1950s and 1960s, such as polyethylene and polypropylene, which were cheaper and easier to produce.
- Plastic pollution became a concern as plastic waste accumulated in oceans and landfills, leading to efforts to reduce plastic consumption and increase recycling.
- Biodegradable and compostable plastics were developed in the 1970s as more sustainable alternatives to traditional plastics.
- Plastic's impact on capitalism is complex, providing efficiency and profitability but also contributing to unsustainable practices.
- Plastic has been portrayed in movies, fashion, and literature, reflecting its cultural significance.
- Efforts are underway to address the negative impacts of plastic and develop a more sustainable future with bioplastics and improved recycling practices.

Interesting Questions

- When did scientists start experimenting with chemicals and natural materials to create a substitute for ivory and tortoise shell?
- Who invented Bakelite and in what year?

- How did plastic production increase during World War II and in what applications was it used?
- What are some examples of plastic products that were introduced in the mid-20th century?
- What are some challenges faced by bioplastics and biodegradable plastics?

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