

LONG-TERM PROPERTIES AND END-OF-LIFE OF POLYMERS FROM RENEWABLE RESOURCES

J.D. Badia^{1,2,*}, O. Gil-Castell¹, A. Ribes-Greus¹

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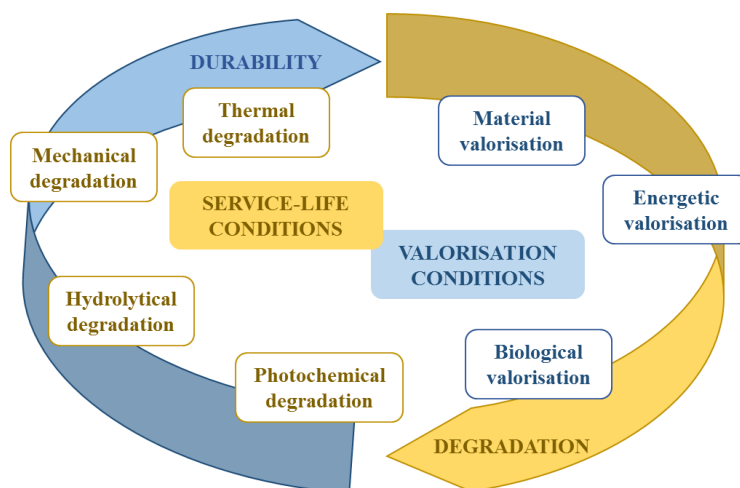
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Abstract

The long-term properties and end-of-life of polymers are not antagonist issues. They actually are inherently linked by the duality between durability and degradation. The control of the service-to-disposal pathway at useful performance, along with low-impact disposal represents an added-value. Therefore, the routes of design, production, and discarding of bio-based polymers must be carefully strategized. In this sense, the combination of proper valorisation techniques, i.e. material, energetic and/or biological at the most appropriate stage should be targeted. Thus, the consideration of the end-of-life of a material for a specific application, instead of the end-of-life of a material should be the fundamental focus. This review covers the key aspects of lab-scale techniques to infer the potential of performance and valorisation of polymers from renewable resources as a key gear for sustainability.

Graphical abstract



Keywords

long-term properties; durability; stability; end-of-life; degradation; material valorisation; energetic valorisation; biological valorisation; bio-based polymers; renewable resources;

Highlights

- The long-term properties and the end-of-life of polymers are not antagonist issues
- The duality between durability and degradation is key for the sustainable design
- Design, production, valorisation and disposal of bio-based polymers are strategic
- End-of-life of a material for an application, instead of end-of-life of a material
- Material, energetic and biological valorisations must be smartly combined.

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List of abbreviators

AFM	Atomic Force Microscopy
AIDS	Acquired Immune Deficiency Syndrome
ASTM	American Society for Testing Materials
ATP	Adenosine Triphosphate
DETA	Dielectric Thermal Analysis
DMTA	Dynamic Mechanical-Thermal Analysis
DSC	Differential Scanning Calorimetry
EN	European Standards Organisation
FTIR	Fourier Transformed Infrared Spectroscopy
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HV	Hydroxyvalerate
ISO	International Standard Organisation
LCA	Life Cycle Assessments
LMWC	Low Molecular Weight Compounds
MALDI-TOF-MS	Matrix-Assisted Laser Desorption-Ionization Time-of-Flight Mass Spectrometry
MODA	Microbial Oxidative Degradation Analyser
NMR	Nuclear Magnetic Resonance
OIT	Oxidation Induction Time
PBAT	Poly(butylene adipate terephthalate)
PBF	Poly(butylene fumarate)
PBS	Poly(butylene succinate)
PCL	Polycaprolactone
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PGA	Poly(glycolic acid)
PHAs	Polyhydroxyalkanoates
PHB	Polyhydroxybutirate
PHBV	Poly(hydroxybutyrate-co-valerate)
PHV	Polyhydroxyvalerate
PLA	Poly(lactic acid)
PLGA	Poly(lactic-co-glycolic acid)
PP	Poly(propylene)
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
PS	Polystyrene
PSW	Plastic Solid Waste
SEM	Scanning Electron Microscopy
TE-EC	End-Chain Transesterifications
TE-MC	Middle-Chain Transesterifications
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TPS	Thermoplastic Starch
UV	Ultraviolet

1. Sustainability of polymers from renewable resources

Plastics currently account for about 20% by volume of municipal solid waste. Even more, they are not only generating so much waste, but are also becoming extinct due to finite petroleum-based reserves. It is estimated that the global resources of oil, natural gas and coal are limited and the economic impact could be exhausted in a near future, as prices will rise as these resources are more limited [1]. Due to the oscillation of oil prices and the problem of the accumulation of waste, which has led to hard environmental policies, polymers from renewable resources may become a sustainable solution. Actually, this market has experienced a high expansion, being the focus of lots of research studies [2], in many sectors of application, such as food packaging, agriculture and biomedicine, among other.

Food packaging applications aim at substitute traditional polymers [3] [4] by bio-based polymers such as poly(lactic acid) (PLA) [5]–[8] or polyhydroxyalkanoates (PHA) [9], [10], along with other polymers [11]–[13], blends [14]–[16], or nanocomposites [17] [18]–[21] [22] [23] [24] [25]–[27] [28] [29], [30] [31]. The focus is devoted to the combination of appropriate processability, good durability [32], [33] [34] barrier properties [35] [36] [37] [38] [24] [39], [40] and tuned biodegradability [33], [41]–[46], as well as to add value with natural additives [47], the combination of coatings [48] [35] [36] [49] [50]–[56] [57], [58] and multilayers [37] [38] [59] [60] [61] [62] [63] [31] [64], [65], or even the production of edible [66] [67] [68] [69] [70] [58], [71], [72] [57], [58] [73] [74] or active properties [75] [76] [77] [78] [79] [80] [81] [82], [83] [84] [85] [86] [87]. Agricultural applications [88] consider the use of polymers from renewable resources as films for mulching and protection [88] [89] [90] [91] [92], drug delivery [93], [94] [95]–[98] [99] [100] [101] [102], [103] or goods as twines, strings, filaments and clips [104]. Biomedical applications based on polymers from renewable resources [105], [106] are based on their biodegradability and biocompatibility with low-impact form substance after degradation [107] [108] [109], for applications such as tissue engineering [110]–[112] [113] [114] [115] [116] [117], [118] [119] [120] [121], which ensure cell proliferation [122]–[124] [119], [125]–[128], controlled drug delivery [129], [130] [131]–[135] [136], [137] [138]–[140] [141] [142], wound dressing [143] [144], [145] [146]–[148] [149], [150] [151]–[156] [157] [158], [159] [117], [160]–[163]. In all cases, all polymers require a tuned balance between their performance during service life, and their degradation behaviour after use, that is, between the long-term properties and their end-of-life. Nevertheless, polymers from renewable resources still involve relatively high production costs and, frequently, they show underperformed properties for each application in contrast to their petroleum-based counterparts. In addition, concerns are growing into the society about the use of long-life polymers in products in which a short-life is expected. Therefore, there is an engagement to base the research in appropriate

production-service-waste management mainstreams on an equitable commitment of the three pillars of sustainability, i.e. People (social pillar), Planet (environmental pillar) and Profit (economic pillar) [164].

Specifically, the sustainability of polymers from renewable resources, i.e. bio-based polymers, is a topic which has been approached from several perspectives due to its importance and impact on wealth, environment and technological development [165]–[170]. Due to their high potential of replacement of petroleum-based polymers, the design, use and disposal routes of bio-based polymers must be carefully strategized in order to ensure appropriate service conditions and adequate valorisation and/or elimination after their service-life [171]. In addition, these processes have to be economically efficient, energetically affordable and environmentally friendly. Thus, the concepts of applications, long-term properties and end-of-life of bio-based polymers have to be constantly linked, as shown in **Figure 1**.

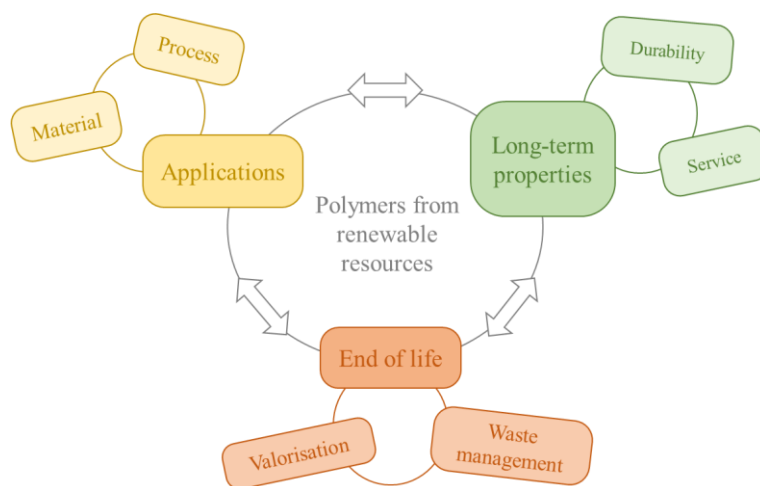


Figure 1. Perspective of this review: interlinked approach of applications, long-term properties and end-of-life of bio-based polymers.

The applications of bio-based polymers are inherent to both the choice of suitable materials and their particular obtaining process to ensure the expected performance during service, which is related to their long-term properties. This combination of process and performance must be efficiently balanced, to guarantee correct end-of-life of the bio-based goods, not only understood as the disposal and reintegration of carbon source into the life cycle, but also from the point of view of its possible valorisations into feedstock, the same or different materials and/or energy. In this sense, in this review, the long-term properties of polymers are approached from the point of view of the durability facing different degrading agents such as temperature, sun light or humidity. The three following sections are devoted to material, energetic and biological valorisations, as alternatives to extend the value of polymers, depending on the expected performance and end-of-life opportunities. Finally, a list of different opportunities to

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foster the background of a correct alignment between long-term properties and end-of-life is proposed, in order to contribute to the field of sustainable design of polymers from renewable resources.

2. Long-term properties and end-of-life of polymers

The terms durability and degradation, as well as long-term properties and end-of-life are inherently linked. The emphasis on each term will be showed depending on the focus of the analysis under consideration. Whether the conservation of the high-level performance of bio-based polymers is aimed, the preservation of its durability will determine the improvement of long-term properties. On the contrary, if the elimination of plastic waste after discarding is sought, monitoring and favouring the most effective degradation pathway will be focused. However, both ideas are not antagonist. In fact, both must be considered together at the steps of design or choice of appropriate materials for specific applications. A correct balance between an appropriate durability of a plastic good and a simple end-of-life pathway without energetic or environmental impact should be addressed. Even more, the consideration of the end-of-life of a material for an application, instead of the end-of-life of a material should be kept in mind in order to favour second-life uses, and thus enlarge its service-life, giving an extra value to this material. Sending discarded material to downgraded applications, combine them with other materials to upgrade them, obtaining energy, feedstock or recover the carbon sources by biological methods should be considered as added-value alternatives for bio-based polymers.

Different strategies to simulate service-life conditions, and thus focus on the durability of the materials, or to simulate different valorisation options, therefore aiming the degradation pathways, can be taken into account, as schematised in Figure 2.

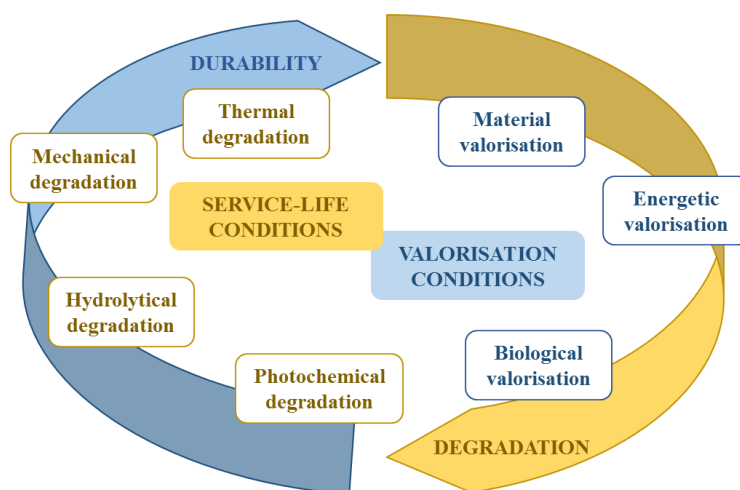


Figure 2. Types of durability and degradation studies summarised in this review.

The physico-chemical properties of bio-based materials subjected to different service-life or valorisation conditions must be followed in order to respectively evaluate, on the one hand, the preservation of performance or, on the other hand, to monitor the extent of degradation to ensure correct valorisation. In this sense, as shown in Figure 3, the evaluation of properties goes from

micro-approach, i.e., structure-morphology, to macro-response, i.e. mechanical, thermal or rheological properties, connecting with the application at the durability stage, and with the surroundings and impact on environment and human health with the analysis of release of low-molecular weight compounds, at the degradation stage.

Structural and morphological observation by means of techniques such as Gel Permeation Chromatography (GPC) [172], Matrix-Assisted Laser Desorption-Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS) [173]–[175], Nuclear Magnetic Resonance (NMR) [176], or Fourier-Transform Infrared Spectrometry (FTIR) [177] are used for determining the molar-mass distributions and to identify the chemical nature of the polymer chains and/or their chemical groups. As well, micrographic techniques such as Scanning/Transmission Electron Microscopy (SEM/TEM) or Atomic Force Microscopy (AFM) allow the observation of the topology of polymers as well as the analysis of interfaces in blends or composites [178]. In addition, Differential Scanning Calorimetry (DSC) can be used to determine the main thermal properties and the balance between crystalline and mobile and rigid amorphous fractions [179], [180]. As well, Dielectric Thermal Analysis (DETA) and Dynamic-Mechanical Thermal Analysis (DMTA) is of great importance to test the segmental rearrangements and dynamic fragility of polymers [181]–[184], which modifications are not perceptible by other macroscopic techniques.

The macroscopic response, in terms of rheological, thermal and mechanical performance is of great importance and currently the focus of most reports, due to the technology-driven and market-pulling of applications for bio-based polymers. The mechanical characterization of the stress and strain at break or impact to check the resistance of second-life applications is fundamental. The control of the rheological properties in order to assure proper flow during processing, as well as the study of the stability indicators such as the Oxidation Induction Time (OIT) or the Temperature of Oxidation (T_{Ox}), the thermal and thermo-oxidative decomposition temperatures or the melting temperatures are of immediate application and use in industrial quality labs to infer the necessary processing windows. In addition, those polymers designed for specific applications need specific analyses which may inform about the suitability of these materials to be used in second-life applications or should be sent to other valorisation routes. This could be the case of polymers used for packaging, which need gas transmission experiments [185]–[187]. As well, those used in electrical or insulating applications may rely on dielectric characterisation [181]. Moreover, for those which serve in contact with food or in aggressive environments, the ecotoxicity should be assessed [188]–[190]. Finally, for those applications in contact with humans, animals, plants or to be used in cosmetics, food packaging or as drugs carriers, for example, the controlled extraction and identification of low molecular weight compounds has to be considered [191], [192].

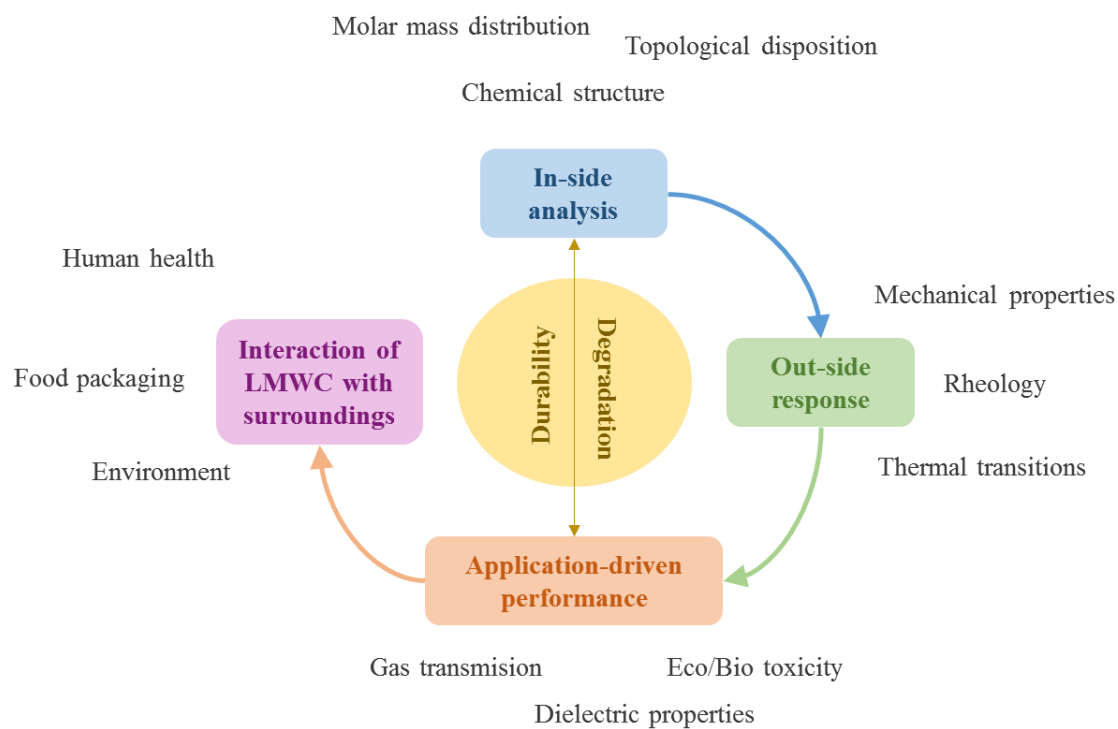


Figure 3. Analytical strategies to monitor durability or degradation.

3. Durability and simulation of service conditions

Bio-based polymers are subjected to different service conditions, which can be more or less aggressive depending on their application, being thus exposed to some degrading factors which individually or in combination can affect their physico-chemical properties, and thus the durability of their properties. In general terms, the types of degradation can be thermal, hydrolytic/chemolytic, photochemical or mechanical. In order to simulate the performance of these materials under these conditions, different normalised and accelerated protocols can be applied.

3.1. Thermal degradation

Thermal degradation comprises the negative response, i.e., loss of properties, due to the subjection of bio-based materials to specific temperatures during extended time. In general terms, one must differ between (i) thermal degradation at temperatures below the glass transition temperature, which can induce structural rearrangements know as physical ageing [193][194][195]; (ii) thermal degradation at temperatures between the glass transition temperature and the melting temperature, which can provoke from loss of dimensions due to flow of material to crystallisation processes or starting of thermal decomposition of low molecular weight additives; (iii) thermal degradation at temperatures above the melting temperature and below the decomposition onset temperature, which will be extremely important to know to ensure processability of second-life bio-based goods, or (iv) thermal degradation above thermal decomposition, which is treated as energetic valorisation option in section 5. In order to test the thermal degradation of bio-based polymers, different methodologies can be used. On the one hand, the use of ovens permits the analysis of every type of thermal degradation, preferably those without decomposition, and then evaluate degradation by analysis of molar masses and physico-chemical properties. Differential Scanning Calorimetry (DSC) is interesting to test thermal degradation at temperatures up to the melting temperature, as well as to monitor degradation by means of indicators such as the glass transition temperature, the degree of crystallinity, the crystallisation and cold-crystallisation temperatures or the crystallinity degree. However, it is not advisable to induce thermal degradation at temperatures below the glass transition by DSC due to the high consumption of time. The use of Dynamic Mechanical Thermal Analysis (DMTA) is suitable to test the impact of thermal degradation until temperatures far below the melting temperature on mechanical properties by means of creep experiments. Finally, the use of Thermogravimetric Analysis (TGA) is essential to test the thermal decomposition of polymer-based materials, both under inert or oxidative conditions. Some studies have been reported for neat [196], [197] and

reprocessed [198] PLA, PLA-based composites [199]–[202], PHAs [203], PCL [204], polyester-based blends [205] or starch-based blends [206], among other.

3.2. Hydrolytic and hydrothermal degradation

Hydrolysis of ester linkages is one of the most established types of bio-based polymer degradation, and therefore most of bio-absorbable polymers for biomedical applications are based on polyesters. There are two main ways by which biopolymers can be hydrolyzed, passively by chemical hydrolysis, or actively by enzymatic reaction. The latter method is more important for naturally occurring polymers such as polysaccharides and PHAs [207]. PLA and PGA degrade by simple hydrolysis of the ester bond and do not require the presence of enzymes to catalyse hydrolysis [208]. The hydrolysis of ester linkages occurs through a series of overlapping stages, progressively reducing the molar mass and thus affecting to the macroscopic physico-chemical properties. Simulation of service-life conditions of biomedical materials usually follows the ISO10993-13:2010 normative [209]. Shortly, materials are exposed to the analytic medium, which can be water, phosphate buffer solution or human fluid simulants, during different times at 37 °C, to mimic human conditions. The monitoring of degradation can be followed both in the liquid and in the solid fractions. Several reports for PLA [210]–[213], PCL [214], PHAs [215], poly(butylene fumarate) (PBF) [216], or copolyesters [217] can be found in literature, among others.

For non-biomedical purposes, modified water absorption protocols such as the ISO62:2008 [218] can be used to induce accelerated hydrothermal degradation on polymers. In this sense, both agents, water and temperature can synergically act to simulate real service conditions. This has been reported for neat [219], [220] and reprocessed PLA [221], [222], PHAs [223], [224], PCL, and blends [225] or composites such as PLA/sisal [226], [227], PHBV/sisal [228], or poly(butylene sebacate) (PBS)/montmorillonite [229], among others.

4.3. Mechanical degradation

Bio-based polymers can be subjected to several types of mechanical solicitations during processing, storage and use. These mechanical stresses can be tensile, compressive, shearing or bending, in the form of vibrations, agitations, grinding or hard extrusion.

The basic phenomenon involved when subjecting the polymer to very powerful shearing forces is the breakage of the macromolecule. Mechanical degradation reduces the average molecular weight of the polymer [230]. Although mechanical factors are not predominant during biodegradation, they can activate or accelerate it [208]. In order to simulate mechanical degradation, common experiments of fatigue or creep can be performed on polymers by DMTA

[184], which not only serve for classical mechanical analysis, but also gives the chance of applying several vibrating frequencies and combine them with thermal effect.

4.4. Photochemical degradation

Photodegradation of polymers is induced by the action of light, due to UV absorption, mainly by carbonyl groups of polyesters [231]. Photodegradation mechanisms are mainly expressed by the Norrish reactions that transform the polymers by photoionization (Norrish I) and chain scission (Norrish II) [232]. Photodegradation can conduce to Norrish reactions and/or cross-linking reactions, or oxidative processes [233]. Polymers such as PLA or PCL [234] have shown Norrish-type photodegradation, whereas others such as Poly(butyrate adipate terephthalate) (PBAT) or Ecoflex® have shown main routes of cross-linking and chain scission [235], [236].

Photodegradation and sunlight oxidation test protocols are practices such as ASTM D5071 with Xenon lamps [237], ASTM D5208 with fluorescence lamps [238], or ASTM D5272 for outdoor conditions [239] are preferably used for exposing a plastic to some form of radiation and subsequently measuring the loss of any property, usually molar mass and mechanical properties, such as tensile or impact resistances or show the performance of additives to protect them such as ZnO [240], Si colloids [241] and other stabilizers to prevent them from degradation [242]. These techniques allow setting not only UV wavelengths, but also temperatures, day-night cycles, or controlled floating, rain or humidity. Some studies have been reported for neat PLA [196] and composites [243]–[245], PHAs [246]–[248], PCL [234], starch-based blends [249], [250] or cellulose [251], [252], among others.

4. Material valorisation of biopolymers

Short-time applications from bio-based and biodegradable plastics have attracted much interest in different industrial, social and economic sectors [253]. It is known that bio-based materials are suitable for biological waste treatment such as composting, thus having a great potential to contribute to the reduction of the amount of waste sent to landfill and generating valuable soil improvers, which is of great importance for industries, governments and consumers [254]. However, the presumably high amount of bio-based plastic waste surpassing the capability of composting facilities has to be taken into account [255]. Actually, including the end-of-life stage in Life Cycle Assessments (LCA) provides more comprehensive life pathways for bio-based polymers, but simultaneously introduces greater amounts of uncertainty and variability. Although there is little life-cycle data available on the impacts of different ways of disposal, it has been argued that it would be critical for future sustainability assessments [256], [257]. The necessary implementation of operation units during the dismantling process, new separation technologies, and the logistics of handling additional streams of materials will require significant study, development, and monitoring in order to develop robust and effective recovery methods [258]. In this sense, to explore the chances to enhance the valorisation of bioplastic-based goods, by means of mechanical recycling would be advisable to explore the possibilities of extending their service lives before finally discarding them to bio-disposal facilities [259], [260].

Mechanical recycling represents one of the most cost-effective methodologies, though recycled materials are usually directed to downgraded applications, due to the inherent thermo-mechanical degradation affecting its mechanical, thermal and rheological performance [261]. During re-processing, polymers are subjected to the synergic influence of degrading agents such as oxygen, UV-light, mechanical stresses, temperature and water, which, separately or in combination, during its material loop (synthesis-processing-service-life-discarding-recovery), results in chemical and physical changes that alter their stabilization mechanisms and long-term properties [262], [263]. Degradation usually provokes a reduction of physical properties and functional quality of polymers and, hence, reprocessed products of high confidence are difficult to obtain. Traditional simulation of mechanical recycling by multiple processing and service-life by accelerated thermal ageing was previously developed for commodities such as PE [264], PP [265], poly(styrene) (PS) [191], [192], poly(vinyl chloride) (PVC) [266] or PET [179], [267]–[269], among others. Concerning bio-based polymers, the main effort has been dedicated to PLA in great extension, and other materials such as PHAs [270]–[272], poly(caprolactone) [273] or biocomposites with matrixes of PLA or thermoplastic starch (TPS) [274].

The mechanical recycling of PLA has been approached in lab-scale studies by means of multiple injection [183], [275]–[277] and extrusion [278]–[281] steps, and the recyclates characterized in terms of structural and morphological analysis rheological, thermal and mechanical properties, release of low molecular weight compounds (LMWC) [282], and application-driven techniques such as mass-transport [221] or dielectric properties [181]. A review devoted to the mechanical recycling of PLA [261] showed that, in general terms, reprocessing of PLA was responsible for a decrease in molecular weight, modification of thermal properties and crystallization kinetics, dynamic fragility or permeation performance, among other parameters [261]. As a general idea, PLA could be reprocessed without losing most of its properties up to 2 cycles, but this affirmation strongly depends on the PLA grade used and the care during reprocessing. Studies focused on the characterization of multi-injected PCL have revealed that PCL technological waste is suitable to be reused as an additive to a neat polymer [273]. Regarding PHAs, their performance of mechanical recycling was tested during successive injection [270], [271] and extrusion cycles [272], showing successive diminution of molecular weight after increasing cycles, with its consequent decrease in mechanical properties.

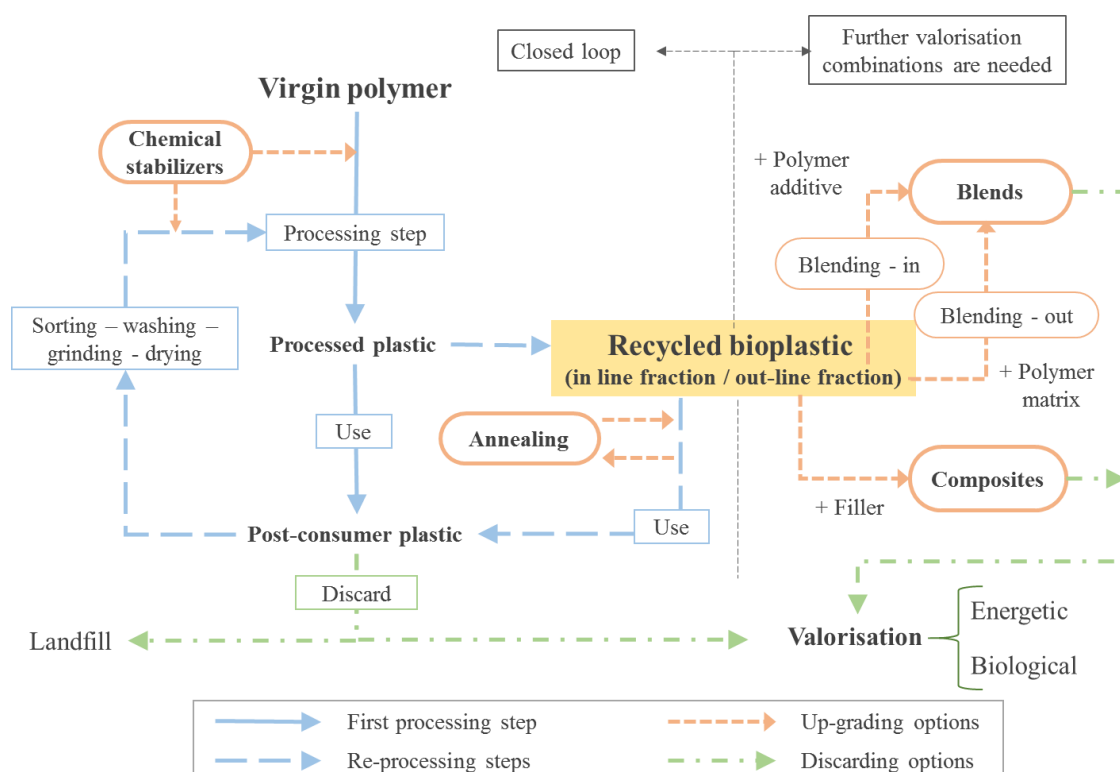


Figure 4. Scheme of material valorisation through mechanical recycling and up-grading options.

Figure 4 shows a schematic material flow from virgin to recycled polymer in a closed loop, i.e. within the same polymer fraction, or in combination with other material, which hinders the continuation of material flow inside the mechanical recycling loop and thus suggests the design for further valorization. Due to degradation during re-processing, the performance of

bioplastics is usually downgraded and thus several strategies to improve and upgrade materials can be followed. This is the case of the application of physical treatments such as annealing to increase young modulus and yield strength of PLA [275], [283] or the use of chemical stabilizers such as tropolone, quinones or irgafos/irganox during processing to prevent transesterification [284], [285]. Other options include the blending of recycled polymers with other ones that can act as plasticizers or tougheners (blending – in) [277], [286]–[288], or the use of recycled bioplastics as value-added modifiers for other plastic matrixes (blending – out) [289]–[291]. The case of the combination of PLA and PHBV is remarkable [272]. The effects of 6 recycling cycles on the structure and properties of neat PHBV, neat PLA and PHBV/PLA (50/50 wt%) blends elaborated by injection moulding were investigated. In contrast to PLA, PHBV seems to be relatively more sensitive to the thermomechanical degradation, where the presence of PLA in the PHBV–PLA blend tends to partially prevent the degradation of PHBV. Even more, it was suggested that the recyclability of PHBV/PLA blends was affordable after several reprocessing cycles, since the values of mechanical properties remained at the original level, as well as the molar mass slightly reduced [272]. Other studies focused on blends such as that of PLA/TPS have shown worsening of the thermal properties as a function of reprocessing cycles, especially for those with high concentration of TPS [292].

Finally, the option of compositing recycled bioplastics following the same compositing routes as for neat polymers may also provide with upgraded performance. *Lopez et al.* studied the recycling ability of biodegradable matrices such as PLLA and Mater-Bi and their cellulose-reinforced composites in a plastic recycling stream [293]. In the same direction, the behaviour of polylactide/flax composites was evaluated after several recycling cycles [294]. Moreover, polylactide-recycled wood fibre composites were prepared and characterised by *Pilla et al* [295]. Other applications of reused natural fibre reinforced composites such as in polymer mortars were considered by *Grozdanov et al* [296].

Once the extent of material valorisation has been exhausted, there are still possibilities to make profit from bioplastics without the need of sending them to landfilling. This is the case of energetic or biological valorisation, as shown in the next sections.

5. Energetic Valorisation of Biopolymers

Energetic valorisation is compressed under the term chemical recycling, which covers both chemical methods to recover feedstock from wastes and thermolytic processes to obtain energy. Figure 5 shows the relationship between these technologies put in practice.

Feedstock valorisation refers to advanced technological processes which convert plastic materials into smaller molecules, usually liquids or gases, which are suitable for being used as a feedstock for the production of new petrochemicals and plastics. The technology behind its success is the depolymerisation –both chemically and thermally driven– process that can result in a profitable and sustainable industrial scheme, providing a high product yield and minimum waste [297]. However, for the case of bioplastics, the effort in recovering monomers could be more expensive and harmful for the environment than just obtaining them as raw material. Concerning the energy balance and costs, these processes lay between re-melting and combustion [298]. In fact, chemical recycling options could be suitable when the amount of wastes surpass the capabilities of biological valorisation facilities. More literature of feedstock recycling can be found in terms of chemically-driven obtaining of lactic acid by hydrolysis of PLA [299]–[301] and thermally-driven obtaining of L-L-lactide from PLA [302]–[304] or vinyl monomers from PHAs [3]. It must be pointed out that feedstock recycling might be particularly interesting for blends of biopolymers with commodities when high performance at service conditions is no more expected, especially for those difficult to separate mechanically, or those which have different thermal decomposition profiles. This could be the case of blends of PHBV/PE [305], PLA/PET [306], PLA/PE [307], [308] or PLA/PBS [309].

Energetic valorisation implies thermal cracking of waste to produce energy in the form of heat, which may be converted into steam and further to electricity by a conventional thermoelectric plant. Polymer-based materials possess a very high calorific value when burned, especially when considering that they are derived from crude oil. Since the heating value of plastics is high, they make a convenient energy source, such as heating oil and coal [310]. Thermolytic processes consider pyrolysis, gasification, combustion, liquid–gas hydrogenation, viscosity breaking, steam or catalytic cracking, and the use of plastic solid waste as a reducing agent in blast furnaces [311].

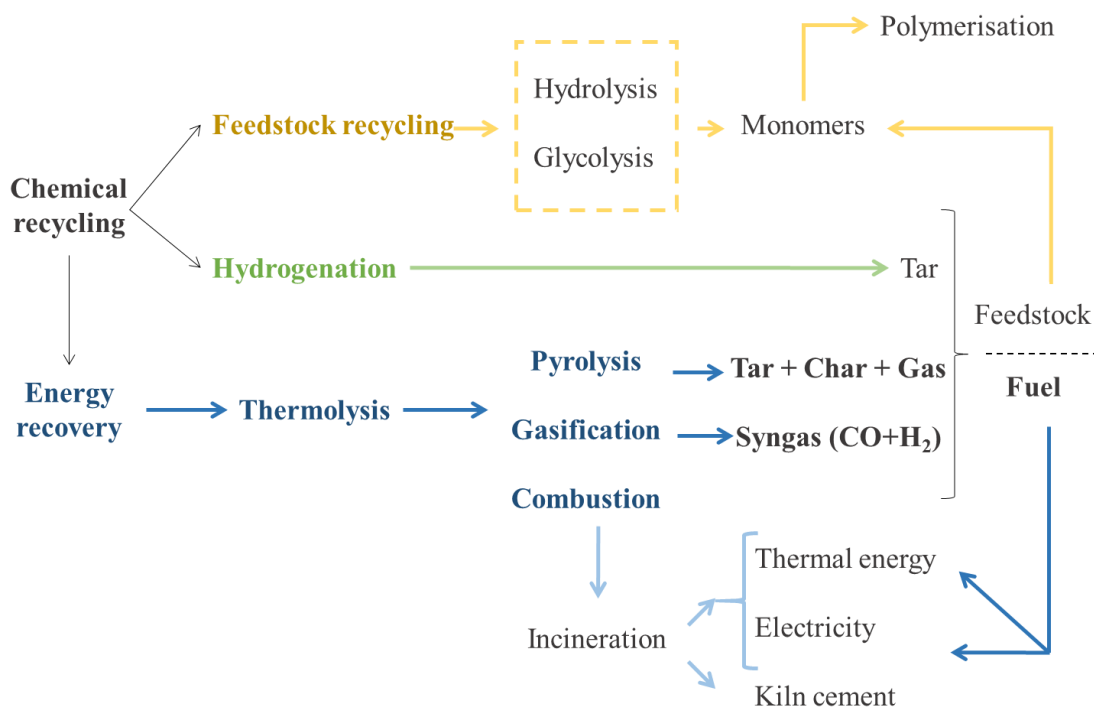


Figure 5. Chemical recycling options. Detail of thermolytic processes for energetic valorisation. Redrawn from ref [255].

Not only healthy monomer fractions can be recovered up to 60% [312], but also valuable petrochemicals can be produced, such as gases (hydrocarbons), tars (waxes and liquids very high in aromatic content) and chars (carbon black and/or activated carbon). However, one must consider that, in general, post-consumer plastic waste consists of a variety of long chain polymer molecules, chemical contaminants and hetero-atoms such as chlorine, oxygen or nitrogen. Physical impurities like fillers, pigments or adhered dirt are present as well as larger inorganic material, arising from incomplete sorting. In order to use this waste as feedstock for new plastics or fuel components, the following problems need to be overcome [313]: (i) Larger inorganic particles have to be discharged from the process in order to prevent the process to be blocked by, as well as to avoid the erosion of pipes and pumps; (ii) Inorganic particles have to be mechanically separated; (iii) Long polymer chains have to be cracked; and (iv) Hetero-atoms need to be chemically separated.

5.1. Pyrolysis, gasification or combustion

Pyrolysis has the ability to produce high calorific value gas by thermal cracking in inert atmospheres at temperatures up to 800 °C [313]. The solid char can be used in-site to release its energy content by further thermal processes or used off-site to valorise its inorganic residues in further applications. In contrast to other thermolytic technologies, pyrolysis has the advantages of being less energy consumer, using low pressures and preventing the generation

of pollutants [311], [313]. Examples of pyrolysis for Plastic Solid Waste (PSW) [312], biomass [314] or rubbers [315] have been reported. Of all the biopolymers investigated, PHB is the most promising material, followed by aliphatic-aromatic copolyesters, PLA-based polymers, potato starch, corn starch and starch based biopolymers in order of decreasing profits [208], [316]–[319].

Gasification operates at temperatures up to 1300 °C and use controlled addition of oxygen as reagent [313]. It mainly produces syngas, which is a mixture of carbon monoxide and hydrogen, which can be used as fuel, substituting natural gas. Additionally, a significant amount of char is produced which has to be further treated. If this inorganic ash is bounded into a glassy matrix, it can be used as a component in concrete or mortar due to its high acid resistance [313]. As well, the emission of pollutants is reduced due to the use of high temperatures and low oxygen partial pressure in its operational parameters [313]. Some applications of gasification of conventional plastic fractions have been developed for PVC [320], PP [321] or PET [322], as well as for bio-based polymers such as PLA and others [323]–[325].

Incineration involves the combustion of polymer wastes to obtain mainly carbon dioxide, water and inorganic ashes. Despite the unpopular not-in-my-backyard syndrome, its use as centralized alternative for landfill could be significant, considering that the technologies of control of pollutants are efficient enough. In fact, it could be advisable for not-recoverable plastics coming from biomedical applications, drugs, hazardous-goods packaging, electronics or highly contaminated plastics. The inorganic fraction of the waste, if any, is essentially mineralised in an inert slag that can be used in cement kilns for materials for construction of roads.

5.2. Tests to approach the pyrolysis and combustion of bioplastics

Appropriate design and scale are of paramount importance when it comes to thermal treatment plants. Thermolysis behaviour in laboratory scale enables the assessment of a number of important parameters, such as thermal stability temperature of polymers, thermal kinetics, activation energy assessment or product formation [311].

To design a chemical reactor, the expression for the decomposition rate must be ascertained. Assuming the reaction is known not to be elementary, the search for a mechanism that describes the reaction taking place or use experimental data directly must be aimed. Mechanisms can be hypothesized as the sum of a series of elementary reactions with intermediates. Using methods developed by physical chemists, whether the proposed mechanism fits the actual experimental evidence can be hypothesized. Systems kinetics will not only develop appropriate models that will predict systems products and their interaction, but through solving the derived mathematical expressions, they will predict the product interaction behaviour. This will assist

in reducing side reactions and undesired by-products on an industrial scale. Developing rate expressions of the materials being treated will then be utilized in determining the optimum unit operation to be used and its required supply of power and proper media of operation, in the case of pyrolysis, the sufficient amount of inert atmosphere in the pyrolyser or the ratio of steam to oxygen in a gasifier [326].

In the attempt of developing a model for thermal and thermo-oxidative decompositions in full-scale systems, the main purpose is to describe the behaviour of polymers in terms of intrinsic kinetics, in which heat and mass transfer limitations are not included. General kinetic models are proposed in literature for plastics and biomasses [327]. These models do not take into account the rigorous and exhaustive description of the chemistry of thermal decomposition of polymers and describe the process by means of a simplified reaction pathway. Each single reaction step considered is representative of a complex network of reactions [328].

Pyrolysis is usually the first process in a thermal plant. This could be approached via the understanding of the systems kinetics by Thermogravimetric Analysis (TGA) and scale pilots, using inert atmospheres such as Ar or N₂. Combustion/Gasification systems can also be approached by using O₂ or mixtures of N₂/O₂ rich in the O₂ phase [311]. Therefore, TGA stands out as fast, cost-effective and reliable characterization technique to ascertain a deeper knowledge about the ongoing thermal and thermo-oxidative decomposition of plastics. Completing this experimental technique with a proper theoretical model-fitting methodology is commonly used for the study of kinetic parameters such as the apparent activation energy E_a , the pre-exponential factor A and the reaction model $f(\alpha)$, which yield the so-called kinetic triplet [329], [330]. The hyphenation with techniques such as GC-MS or FT-IR for identification and quantification of gases [331], as well as the use of 2D-correlation spectroscopy to set the sequences of release of gases complete the analysis [330], [332], [333]. These parameters are essential to further optimise the design of the thermal valorisation processes in computer simulation software to achieve a better understanding of the process to obtain the optimum operational parameters in a thermal equipment [329], [334].

5.3. Thermal decomposition studies of bioplastics

Applications of TGA to model thermal decomposition of bioplastics are reported for PHAs [203], [335]–[340], PLA [276], [333], [341]–[343], PCL [344]–[348], celluloses [349]–[352], and chitosan [353], among others.

Studies on PHAs showed that their thermal decomposition occurred through a simple reaction mechanism [335]. This supported the hypothesis that the controlling step was the

depolymerization of the macromolecular chains. The results clearly indicated an increase in activation energy with increasing hydroxyvalerate content.

Concerning decomposition of PLA, *Kopinke* and *Mackenzie* [354], [355] surveyed previous studies and concluded that the thermal decomposition of PLA is mainly driven by transesterification and homolytic reactions, as shown in Figure 6 and Figure 7, respectively and, with minor participation, catalyser (Sn)-based depolymerization or cis-elimination.

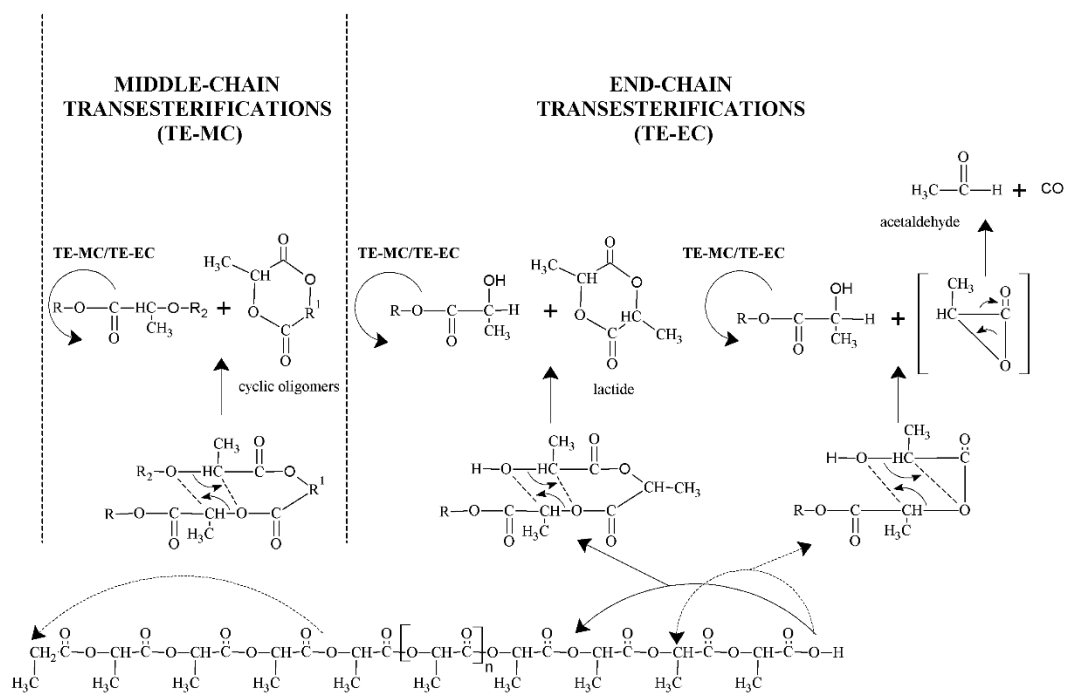


Figure 6. Transesterification reactions of thermal decomposition of PLA, as adapted from [356]. Note that R is an undefined PLA chain fraction.

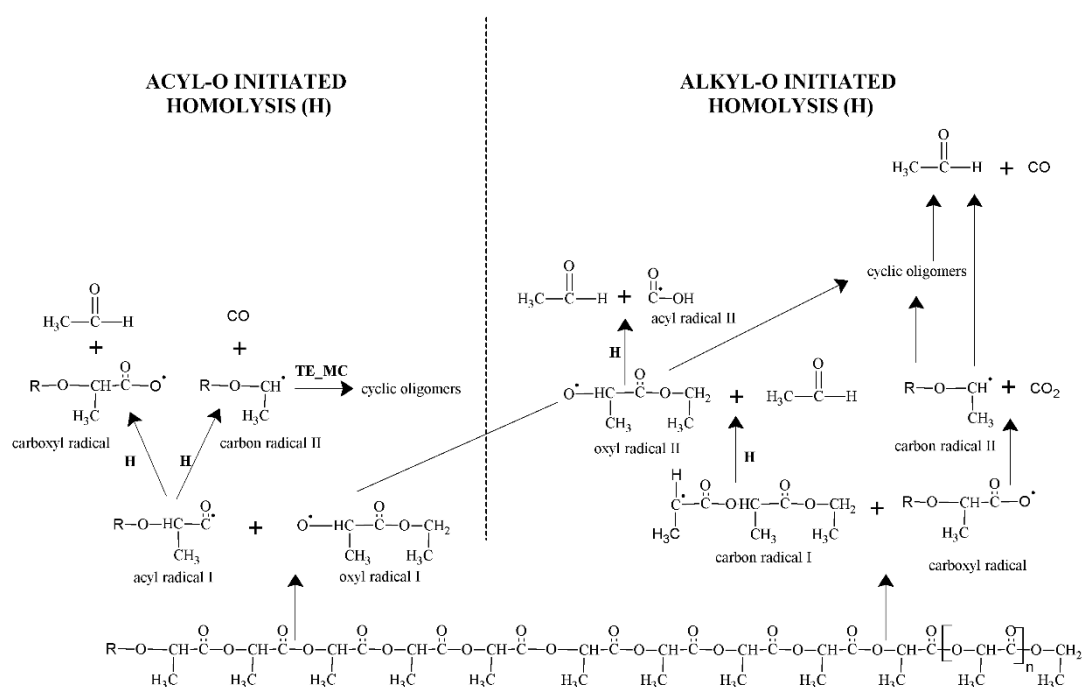


Figure 7. Homolytic reactions of thermal decomposition of PLA, as adapted from [354]. Reproduced with permission from [255]. Note that R is an undefined PLA chain fraction. TE-MC stands for middle-chain transesterifications.

Combinations of valorisation procedures of PLA have been considered. This is the case of the thermal simulation of the decomposition process of recycled PLA [333]. It was found that PLA, as well as its successive recyclates, described a mass-loss profile driven by one decomposition stage in inert conditions and two in oxidizing conditions. In both cases, the first step could be ascribed to the pyrolysis of the backbone. The second mass-loss step under O_2 was related to the decomposition of the remaining char, representing a $\sim 2\%$ of mass. The mathematical description of the kinetics allows technicians to use mechanically-recycled PLA as raw PLA in thermally-driven energetic valorisation facilities.

The thermal decomposition of PCL was investigated in bulk and solution by *Sivalingam* and *Madras* [344]. They found that the polymer degrades by random chain scission and specific chain end scission in solution and bulk, respectively. The activation energy of the processes, determined from the temperature dependency of the rate coefficients, was found to be significantly higher than that of the degradation in solution. The use of several strategies to modulate and tune the thermal decomposition of biopolymers such as PCL are of great importance, as demonstrated by *Albertsson et al.*, who enhanced the degradation of PCL through the incorporation of recycled oxidized model polyethylene powder as a filler in polyethylene/polycaprolactone blends [357].

The thermal decomposition of cellulose over the wide range of mass loss is essentially the same in both air and nitrogen. At the beginning of the decomposition, oxygen interacts only with surface cellulose, resulting in only $\cong 3\%$ of mass loss. The two-phase model of cellulose was proposed to explain all observable phenomena related to both the pyrolysis and the oxidative decomposition. According to the report of *Mamleev et al.* [349], the decomposition occurred through a migration of chain ends from the phase of polymer cellulose into the phase of products, i.e. char, gases and high-boiling tar.

6. Biological valorisation of biopolymers

In contrast to previous sections, this one deals with the valorisation of plastics from the point of view of the reincorporation of polymers into the Carbon cycle under biotic conditions. The design of plastic materials from renewable resources for high-consume applications such as packaging or agricultural mulches moves towards the design of sustainable polymers with controlled degradability and enhanced bio-reintegration. Cradle-to-cradle design enables the establishment of completely beneficial industrial systems driven by the synergistic search of positive economic, environmental and social goals by enabling a perpetual flow within both biological and technical metabolisms [358]. Although certain biodegradable polymers can be used in long-term applications, the commercialization of these materials is continuously increasing in markets for products that have a short lifetime. Biodegradable polymers are much beneficial when they can actually biodegrade in the environment [359]. Thus, the understanding of the degradation mechanisms, as well as the standard methodologies to test the biodegradability of natural polymers by microorganisms and enzymes should open new prospects in the field of biodegradable plastics [360].

6.1. Steps of biodegradation

Biodegradation of plastics occurs through non-competitive and likely-coincident stages, which erode and disintegrate the polymeric segments by depolymerisation, being the cleavage chains reintegrated into the carbon cycle by assimilation and mineralisation in the media. Three main stages can thus be distinguished: deterioration, fragmentation and assimilation.

The deterioration of biopolymers could proceed through bulk or surface erosion [360]. In the case of bulk erosion, fragments are lost from the entire polymer mass and the molar mass decreases due to bond cleavage. This breakage is provoked by chemicals such as H₂O, acids, bases, transition metals and radicals, but not by enzymes, since they are too large to penetrate throughout the matrix framework. In the case of surface erosion, matter is lost but there is no relevant change in the molar mass. One should note that if the diffusion of chemicals throughout the material is faster than the cleavage of polymer bonds, the polymer undergoes bulk erosion. In contrast, if the cleavage of bonds is faster than the diffusion of chemicals, the process occurs mainly at the surface of the matrix.

The fragmentation of biopolymers is considered when low molecular weight molecules are found within the media [360]. The fragmentation is a lytic phenomenon necessary for the subsequent assimilation of the broken polymeric chains into the surrounding environment. Fragmentation is fundamentally an electron transfer process [361]. Biological energy is obtained through the oxidation of reduced materials, where the enzymes catalyse the electron

transfer. The loss of oxygen induces a change in the activity and composition of the soil microbial population. Facultative anaerobic organisms can use oxygen, when it is present, or can switch to alternative electron acceptors, such as nitrates and sulphates [361].

The assimilation is the unique event in which there is a real integration of atoms from fragments of polymeric materials inside microbial cells, ending up in mineralisation [233], [362]. This integration brings to microorganisms the necessary sources of energy, electrons and elements such as carbon, nitrogen, oxygen, phosphorus, or sulphur, among others, for the formation of the cell structure. Assimilation allows microorganisms to grow and reproduce consuming nutrient substrate, i.e. polymer segments, from the environment. Monomers surrounding the microbial cells must go through the cellular membranes to be assimilated. Inside the cells, the transported molecules are usually oxidised through catabolic pathways conducting to the production of *adenosine triphosphate* (ATP) and constitutive elements of cells structure. The existence of appropriate micro-organisms to synthesize the specific enzymes required to depolymerize and mineralize the targeted polymer is essential. Actually, these two steps in the biodegradation process may not involve the same microorganism. Naturally occurring polymers, such as polysaccharides, proteins, and cellulose, are easily biodegraded since many micro-organisms that produce the enzymes required to metabolize these compounds are readily available in nature [363].

Depending on the microbial abilities to grow in aerobic or anaerobic conditions, there exist three essential catabolic pathways to produce the energy to maintain cellular activity, structure and reproduction [364]–[366]:

- (i) In the case of aerobic respiration, numerous microorganisms are able to use oxygen as the final electron acceptor. These microorganisms need substrates that are oxidised into the cell. Firstly, basic catabolic pathways (e.g. glycolysis, β -oxidation, aminoacids catabolic reactions, and purine and pyrimidine catabolism) produce a limited quantity of energy. Secondly, more energy is then produced by the oxidative phosphorylations performed by electron transport systems that reduce oxygen to water.
- (ii) During anaerobic respiration, several microorganisms are unable to use oxygen as the final electron acceptor. However, they can perform complete oxidation by adapted electron transport in membrane systems. They use final electron acceptors other than oxygen, such as like NO_3^- , SO_4^{2-} , CO_2 , Fe^{3+} or fumarate. The result is also the synthesis of more ATP molecules than in an incomplete oxidation.
- (iii) Fermentation, an incomplete oxidation pathway, is a way to produce energy when the microorganisms lack of electron transport systems and are unsuitable to use oxygen or other exogenous mineral molecules as final electron acceptors. In this case, endogenous

organic molecules synthesised by the cell itself are used as final electron acceptors. The products of fermentation can be mineral and/or organic molecules excreted into the environment, such as CO₂, ethanol, lactate, acetate or butanediol. Frequently, these molecules can be used as carbon sources by other organisms, since they still have a reduction power.

6.2. Requirements for biodegradation

The study of the biodegradation mechanisms should contribute to further developments of the next generation of materials having a high environmental acceptability and recyclability, which would become a powerful tool for the sustainable design of polymers from renewable resources [367]. The requirements for biodegradation of polymers at the fragmentation stage are related to the nature and morphology of the polymer and to the environment of biodegradation, in terms of abiotic and biotic conditions [368].

(i) Concerning the nature of the polymer [369], it must contain cleavable polymer groups, liable to enzymatic hydrolysis or oxidation. The balance among hydrophilicity and hydrophobicity will determinate the velocity of chain scission, being as well faster the lower the molecular weight of the polymers is.

(ii) Regarding the morphology, the amorphous regions are more susceptible to degradation both by enzymatic and non-enzymatic hydrolysis, ascribed to the ease of water penetration into the polymer matrix [367]. Thus, the lack of branching and lower crystallinity enhance biodegradability.

(iii) A well-tuned environment where the specific microorganisms can flourish is essential to assure proper biodegradation. Abiotic factors include appropriate temperature range, presence of H₂O, nature and level of salts, action of oxygen to perform from aerobic to anaerobic modes, trace metals, pH, environmental stability, flux, or pressure [370]. The biotic factors concern the action of specific enzymes, which are catalytic proteins that decrease the level of activation energy of molecules favouring chemical reactions [362].

Several enzymes can be found depending on the class of groups preferred during a given chemical reaction: *oxidoreductases*, *transferases*, *hydrolases*, *lyases*, *isomerases* or *ligases*. Enzymatic hydrolysis and oxidation are the main fragmentation pathways.

(i) The enzymatic hydrolysis is mainly concerned by enzymes that belong to hydrolases, such as *cellulases*, *amylases* or *cutinases*, which are readily synthesised by soil microorganisms to hydrolyse natural abundant polymers like cellulose, starch or

cutin. Regarding polyesters, *lipases* and *esterases* are responsible for the hydrolysis of ester, carbonate, amide and glycosidic linkages [371].

(ii) When the scission reactions by specific enzymes are difficult, e.g. due to crystalline area, hydrophobic zones and steric hindrances, enzymatic oxidation can be implicated [372]. Such is the case of *mono-oxygenases* and *di-oxygenases*, like *oxidoreductases*, which incorporate, one and two oxygen atoms respectively, forming alcohol or peroxy groups that are more easily fragmentable. Other transformations are catalysed by peroxidases leading to smaller molecules. They are hemoproteins, enzymes containing a prosthetic group with an iron atom that can be electron donor or acceptor, i.e. act in both reduced or oxidative ways. Peroxidases catalyse reactions between a peroxy molecule, e.g. H₂O₂ and organic peroxide, and an electron acceptor group as phenol, phenyl, amino, carboxyl, thiol or aliphatic unsaturation [233]. Polymers such as PE, natural and polyisoprene rubbers, lignin and coal are first subjected to biological oxidation by oxidoreductases, such as oxygenases, monooxygenases, peroxidases and oxidases in the biodegradation process [367]. It should be stressed that, though crystalline structures and highly organised molecular networks such as cellulose-based polymer are not favourable to the enzymatic attack, several soil decomposers, particularly fungi, are able to produce H₂O₂ to catalyse the fragmentation [233].

6.3. Standardized methods of analysis

Studies aimed to enhance the suitability and the reproducibility of laboratory methods to assess the biodegradation of polymers are in continuous progression [373]. This is due to the fact that some operative difficulties can arise during the performance of the tests, thus affecting the accuracy of the measurements as based on the monitoring of suited parameters of choice, as well as the outstanding number of new and structurally different renewable polymer materials [188].

Studies are usually performed under land or water conditions. Landfills, compost or soils are used to simulate degradation under land, whereas sewage, marine water or sludge are used to simulate aqueous conditions. All environments furnish different rates of degradation. In fact, it is possible that some polymers that are degradable in one environment may or may not degrade in another environment. In-land experiments might show difficulties during the performance of tests designed to assess the extent of biodegradation as CO₂ release or O₂ uptake in the presence of media such as mature compost. In contrast, the tests carried out in aqueous media are considered easier to set up and generally more reproducible, but are not significant for simulating conditions of buried plastics.

The biodegradation kinetics of a test material under in-land conditions can be influenced by the concentration of the material in the solid medium, as well as by the nature of the microbial populations, whereas the test results might vary significantly depending upon the test duration and a reference material designed in the standard test specifications [188]. A critical discussion has argued that the technical specifications should be rephrased in a unique, condensed and practical norm, in order to avoid confusion between the available normative from different certification agencies with very close characteristics [374].

Several analytical strategies can be considered to test biodegradation of polymers from renewable resources, depending on the stage focused on: deterioration or assimilation.

- (i) Polymer deterioration can be tested by several methods such as the evaluation of macroscopic modifications in the materials, such as roughening of the surface, formation of holes and cracks, changes in colour or development of microorganisms over the surface [375]–[377]. There exist normalised tests to estimate the deterioration by the colonisation of microorganisms on Petri dishes [378]. A positive result of the test is considered as an argument indicating the consumption of the polymer by the microbial species. This way, different microscopy techniques [234], [379]–[381] are used to refine the analysis, along with the study of changes in mechanical, rheological or thermal properties [341], [382]–[384]. In particular, the measurement of the weight loss is frequently used for the estimation of biodegradability, but actually it may not be really representative of a material biodegradability, since this loss of weight can be due to the vanishing of volatile and soluble impurities [226], [228].
- (ii) Polymer assimilation is generally estimated by standardised respirometric methods [385], which mainly consist in measuring the consumption of oxygen or the evolution of carbon dioxide or methane, depending on the respirometric mode. The decrease of oxygen is detected by the diminution of the pressure and may be fully automated. The experiment can be conducted with oxygen limitation or not. In anaerobic conditions, gases are released and the augmentation of the pressure is then measured. The identification of the evolved gases is performed by gas chromatography (GC), infrared analysis (FTIR) [374] or titration [386], [387]. Failure in one test does not necessarily exclude biodegradation, but it merely indicates that under the environmental conditions and/or the timeframe where the experiment was conducted, no or incomplete biodegradation occurred. Thus, more than one test method is usually needed to entirely assess biodegradability.

Table 1 shows a summary of the application of different standards from the American Society for Testing and Materials (ASTM), European Standards Organisation (EN) and International Organization for Standardization (ISO), respectively, on different polymers from renewable

resources of the families of polyesters and polysaccharides. Next sections cover examples of biodegradation studies under in-land and aqueous conditions.

Table 1. Studies based on ASTM, EN and ISO standards on different polymers from renewable resources.

Organisation	Code	Title	Material					
			PLA	PCL	PHAs	Cellulose	Lignin/wood	Starch
ASTM	D5209	Standard test method for determining the aerobic biodegradation of plastic materials in the presence of municipal sewage sludge	[388]	-	[389], [390]	-	-	-
	D5338	Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures	[190], [391]–[393]	[394]	-	-	[395], [396]	-
	D5526	Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions	[397]	[397]	-	-	-	-
	D5988	Standard test method for determining aerobic biodegradation of plastic materials in soil	[391]	-	[248], [398], [399]	[400]	[398]	[102], [401]
EN	14046	Packaging - Evaluation of the ultimate aerobic biodegradability and disintegration of packaging materials under controlled composting conditions - Method by analysis of released carbon dioxide	-	-	-	[402], [403]	-	-
	14806	Packaging - Preliminary evaluation of the disintegration of packaging materials under simulated composting conditions in a laboratory scale test	[189]	-	-	-	-	-
ISO	14852	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of evolved carbon dioxide	[404]–[406]	[405], [407], [408]	[405], [406]	[409], [410]	[411]	[404], [408], [412]
	14855	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide	[190], [393], [404], [413]–[424]	[414], [418], [425]	[426], [427]	[403], [421], [424], [428]	-	[415], [419], [421], [429]–[432]
	16929	Plastics - Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test	-	-	[427]	-	-	[433]
	17556	Plastics - Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved	-	-	[399]	-	[411]	-
	20200	Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test	[35], [185], [434]–[440]	[441]	[185], [434], [435]	[438], [439]	-	-
Review			[188], [233], [256], [372], [373], [442]–[453]					

6.4. Biodegradation under in-land conditions

In-land biodegradation experiments mainly comprise biotic in-soil and in-compost studies [452]. In vitro degradation studies based on the application of microorganisms such as fungi or bacteria are of high interest to tune the binomial soil-bioplactic. Fungal organisms such as *Aspergillus niger*, *Aspergillus flavus*, *Chaetomium globosum* and *Penicillium funiculosum*, as well as bacterial standards such as *Pseudomonas aeruginosa* are suggested in some test protocols according to international standards, and evaluated for growth on suitable plastics, thus correlating them with the susceptibility of the plastic to biodegradation [454], [455]. A list of different microorganisms that have been shown able to degrade different groups of plastics can be found in literature [372]. Compostability covers not only naturally-occurring disintegration and biodegradation understood as the lytic action of microorganisms, but also the application of an accelerated process to favour the conversion of plastics into CO₂, H₂O and cell biomass, with no toxicity [456]. For that reason, high temperature, humidity and aeration systems are used, while the compost proceeds through an initial mesophilic phase, a subsequent thermophilic phase and a final maturation phase.

6.4.1. Aerobic Studies

There are several standardized methods to control and determine aerobic biodegradability and disintegration of plastic materials. Among them, the ISO 14855 is one of the most used norms. This ISO standard specifies a method for determining the ultimate aerobic biodegradability of the plastics, under controlled composting conditions by measuring the amount of carbon dioxide generated and the degree of disintegration of the material at the end of the assay. The test material is exposed to an inoculum derived from compost. Composting takes place in an environment in which temperature, ventilation and humidity are controlled. The test method is designed to provide the percentage of conversion of carbon in the test material that generated carbon dioxide as well as the conversion speed. The method applies to several kinds of materials. For plastic materials from renewable resources, several studies have been published. The most studied materials are those that involve degradation of PLA and its derivatives. In this sense, *Kunioka et al.* proposed the use of PLA powders as the reference test materials for the ISO 14855 methods [417]. They selected mechanical crushing at low temperature of polymer pellets using dry ice for powder production. The degree of biodegradation for this PLA powder was approximately 91% for 35 days. Moreover, they studied the biodegradation of PLA samples in different shapes [414]. Their studies found that biodegradabilities of polymer pellets, polymer films, polymer products and polymer composites in controlled compost could be evaluated according to ISO 14855-2. Final degrees of biodegradation and biodegradation curves of samples prepared from biodegradable polymers with various shapes showed almost

the same tendency. However, *Kale et al.* studied the biodegradability of PLA bottles in real and simulated composting conditions [190]. They found that biodegradation matched well with theoretical degradation and biodegradation mechanisms; however, some variability existed in both conditions, suggesting that the standard methodologies are limited to the plastic material and not to the whole package. On the other hand, *Pantani et al.* studied the influence of crystallinity on the biodegradation rate of injection-moulded PLA [393]. As expected, the crystallinity was found to decrease the PLA degradation rate. The dense structure of the initially crystalline sample was more impermeable to the enzymatic attack and to oligomer diffusion.

Other kind of biodegradable bio-based materials have been studied such as PHAs, PCL, cellulose or starch based materials. For PHBV films, *Weng et al.* worked on the influence of the chemical structure [426]. They compared the degradation behaviour of the homopolymer (PHB) as starting material with copolymer PHBV with several amounts of hydroxyvalerate (HV) units. They found that the higher the presence of HV was, the faster the biodegradation occurred. Moreover, they performed a comparison of the biodegradation in both pilot scale and laboratory scale tests following the ISO14855 standard [427]. The PHBV film was completely disintegrated in the pilot-scale composting test, while the degree of biodegradation was 81% in the laboratory-scale control composting test. Thus, degradation in a semi-real environment at pilot-scale is suggested to be similar while slightly faster than under the standard guidelines.

The biodegradabilities of cellulose, PCL and PLA powders in a controlled compost at 58 °C were also investigated according to the ISO14855 standard [414]. Polymer powder samples were obtained from PCL pellets and PLA pellets by mechanically crushing and sieving. The biodegradations of the samples were measured by the Microbial Oxidative Degradation Analyser (MODA). The reproducibility and repeatability of the biodegradation tests using MODA were confirmed for cellulose powders as the reference material, PCL powders and PLA powders.

6.4.2. Anaerobic Studies

Anaerobic conditions are important for different end-of-life in-land scenarios, such as landfills and anaerobic digestion systems, which are tackled in the section of degradation under liquid media. Conditions in landfills vary considerably in terms of geography, age of waste or management practices [457]. The potential production of CH₄ has been approached in literature from the point of view of greenhouse gas monitoring and, as an added-value alternative, due to its promising performance as a source of energy [458]. In this line, most lab-scale studies have been focused on celluloses and hemicelluloses, due to the traditional presence of paper and cardboard in landfills [459]. Since anaerobic microorganisms have a much limited set of enzymes than under the presence of oxygen, and the energy benefit is lower without presence

of O₂, the rates of degradation are normally lower [460]. Concerning plastic waste, few examples can be highlighted for PLA [388], [461], PHAs [447], PCL [461]–[463], starch/PCL [461], PBAT [461], PBS [463]. It was found that PHB was degraded anaerobically more rapidly than the copolyester PHBV, when tested with either mixed cultures or a single strained isolate, whereas PCL tended to degrade slower than the natural polyesters PHB and PHBV [462]. As well, it was reported that PLA can be considered as a compostable material, being stable during use at mesophilic temperatures, but rapidly degrading during waste disposal in compost or anaerobic treatment facilities. Actually, the biodegradation of PLA was much faster in anaerobic solid state conditions than in aerobic aquatic conditions [388]. Other study showed that anaerobic bacteria degraded PCL-starch blend, showing an 83% biodegradability for 139 days, although its biodegradation rate was relatively slow compared to that of cellulose used as a reference material. Conversely, PBS was barely degraded under anaerobic conditions, with only 2% biodegradability in 100 days [463].

6.5. Biodegradation in aqueous conditions

The study of biodegradation of plastics under liquid environments has to be considered from a double point of view. On the one hand, the design of novel materials to prevent wastes from ships and offshore platforms under seas and oceans, and on the other hand as a faster comparing methodology to test biodegradability of bioplastics. This could be the case of fishery equipment to be biodegradable to reduce harmful impact to sea life if lost during fishing [460].

Different studies have been performed for polymers such as PLA [397], PCL [397], PHB [464] or PBS [464]. In particular, it has been shown that the biodegradability of PCL and PLA powders under aquatic conditions can be tested with sludges at thermophilic conditions (~55°C). The biodegradability of PCL was 92% in the diluted sludge [397]. Other studies at mesophilic conditions (~37°C) showed that bioplastics could be ranked as PHB >> PLA > PCL in terms of anaerobic biodegradation rate, relating it to the detection of the same eubacteria. On the contrary, PBS could not be anaerobically biodegraded by the sludge used in this study [464]. For PHAs, an experiment on PHBV and PE-Starch blends in a freshwater environment showed steady degradation rates of 10–20 mg per day for PHBV even under relatively extreme conditions. Conversely, PE-Starch blends showed no degradation after one year [465]. It was also shown that degradation of PHBV occurred most rapidly in anaerobic sewage sludge, then estuarine sediment, aerobic sewage, soil, and finally in seawater [466]. Concerning microorganisms, it was found that *Pseudoalteromonas* could be isolated as predominant PHBV-degrading bacterium from a tropical marine environment [467].

7. Concluding remarks

Due to their high potential of replacement of petroleum-based polymers, the design, use and disposal routes of bio-based polymers must be carefully strategized in order to ensure appropriate service conditions and adequate valorisation and/or elimination after their service-life. In this sense, the long-term properties and end-of-life of polymers are not antagonist issues, since both are inherently linked by the duality between durability and degradation.

Despite certain biodegradable polymers could be used in long-term applications, the commercialization of bio-based plastics is continuously increasing in markets for products that have a short lifetime. The technological efforts in adding value to these plastic goods are therefore misused. The consideration of the end-of-life of a material for an application, instead of the end-of-life of a material could be therefore kept in mind in order to favour second-life uses, and thus enlarge their service-lives.

Concerning durability, performance tests can be designed to experimentally simulate individual or synergic effects of degrading agents such as temperature, water, chemicals, mechanical stresses or sun light. The control of physico-chemical properties must be monitored in a from-micro-to-macro approach, in order to connect structure to behaviour and, therefore, help decide further steps in the application-to-disposal pathway. Regarding degradation at the end-of-life stage, material, energetic and biological valorisations should be carefully combined. This field is still a matter of interest and offers a wide field of opportunities, as suggested hereby:

(i) Material valorisation would benefit from more specialised sorting technologies for plastic waste, so as the reuse before recycling might be enhanced, as well as the recycled fractions offer more homogeneity in their compositions. As well, the options of using additives, blending and/or compositing to upgrade recycled plastics should foresee the following steps of valorisation and/or disposal. Finally, one should consider that, during real recycling, plastic fractions would be commingled and previously subjected to degrading agents during service life. More standardisation and real-scale studies should therefore be performed for recycled materials, since most are currently run at lab conditions by multiple reprocessing with individual polymers.

(ii) Energetic/Feedstock valorisation could be prioritised after material valorisation when the obtaining of chemicals is relevant and/or the biological facilities cannot cover the treatment of bio-based wastes. Nowadays the studies are devoted, on the one hand, to the analysis of the solid-state thermal and thermo-oxidative kinetics at lab conditions and, on the other hand, to the obtaining of calorific values of bio-based polymers at pilot-scale. In order to link labs with real-scale applications, a current challenge would

be to connect, via computer simulation, solid-state kinetics with operational units such as pyrolysers or gasifiers. The optimisation of working parameters would produce more complete thermal transformation, therefore with higher thermal efficiency and lower emission of gases. This connection would release useful information to set up standards, which may help homogenise the studies and benchmark the applicability of energetic/feedstock valorisation for bio-based polymers.

(iii) Biological valorisation to reintegrate sources into the C cycle is essential for bio-based polymers, obviously for controlled management of wastes via current facilities such as composters and, even more, to ensure the lowest impact of non-controlled disposed bio-based goods. Due to the environmental concern and deep knowledge of the different stages of biodegradation through deterioration, fragmentation and assimilation, and the different media of degradation both aqueous and in-land environments, the amount of standards are sometimes very similar, which complicates the choice of the most appropriate one to certify biodegradation. Therefore, an effort in unifying the standards of certification of biodegradation remains a challenge. As well, the proliferation and optimisation of specific composting facilities for bio-based plastics would help clarify the disposal pathways and therefore reduce the impact of treatment of these wastes.

In conclusion, the balance between the long-term properties and the end-of-life of bio-based polymers is key to set up a design for sustainability. A smart combination of the routes of production, valorisation and disposal might lead to reduce the environmental impact and gear bio-based polymers towards added-value applications.

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Captions

Figure 1. Perspective of this chapter: interlinked approach of applications, long-term properties and end-of-life of bio-based polymers.

Figure 2. Types of durability and degradation studies summarised in this chapter.

Figure 3. Analytical strategies to monitor durability or degradation.

Figure 4. Scheme of material valorisation through mechanical recycling and up-grading options.


Figure 5. Chemical recycling options. Detail of thermolytic processes for energetic valorisation. Redrawn from ref [255].

Figure 6. Transesterification reactions of thermal decomposition of PLA, as adapted from [356]. Note that R is an undefined PLA chain fraction.

Figure 7. Homolytic reactions of thermal decomposition of PLA, as adapted from [354]. Note that R is an undefined PLA chain fraction.

Table 1. Studies based on ASTM, EN and ISO standards on different polymers from renewable resources.

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