Biodegradability of biodegradable mulch film

A review of the scientific literature on the biodegradability of materials used for biodegradable mulch film

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This research project has been carried out by Wageningen Food & Biobased Research commissioned and funded by NRK Verpakkingen, in the context of Literature study on the biodegradability of biodegradable mulch film (project number 6229110400).

Wageningen Food & Biobased Research
Wageningen, March 2021

Public

Report 2138
ISBN 78-94-6395-760-1

Version: final
Reviewer: Karin Molenveld
Approved by: Arie van der Bent
Client: NRK Verpakkingen
Sponsor: NRK Verpakkingen

This report can be downloaded for free at https://doi.org/10.18174/544211 or at www.wur.eu/wfbr (under publications).

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Contents

Summary *(English)*

This report presents the findings of a desk study, commissioned by NRK-V and executed independently by WFBR. The objective of the desk study is to provide insight in the information available in the public and scientific literature regarding the biodegradability of biodegradable mulch film for use in agriculture and horticulture.

Biodegradability of plastic describes the potential to undergo biodegradation in a suitable environment. Biodegradation does not only depend on the chemistry of the polymer, but also on the presence and activity of the biological systems involved in the process. This means that biodegradability in soil can be different from biodegradability in industrial composting conditions.

The biodegradation of plastic is defined as its complete microbial utilization, resulting in its conversion to CO_2, (and/or CH_4), water and biomass by the metabolic activity of microorganisms. Not all materials labelled *'biodegradable', 'oxo-(bio)degradable'* or *'compostable'* will actually biodegrade at sufficient rate at ambient temperatures in soil to prevent accumulation of plastic (residues) in the field.

Typically, mulch films are produced by combining polymeric feedstocks with other components (via master batches), such as processing aids, plasticizers and colorants, which are then further processed through extrusion into film. Regarding biodegradability and environmental fate it is important to consider not only the polymeric constituents, but all components that are used to produce the mulch film.

In this report the biodegradability is discussed of the main polymeric constituents commonly employed for biodegradable mulch film. These include (thermoplastic) starch and several polyesters, including poly(butylene adipate-co-terephthalate) (PBAT), poly(butylene succinate) (PBS), poly(lactic acid) (PLA) and poly(hydroxy alkanoate) (PHA). It is important to realize that general statements regarding the biodegradability of these polymers are not possible, because variations of comonomer composition, molar mass, etc. within a polymer family, can have substantial effects on physical properties and biodegradation behaviour.

Polymer grades that have passed the biodegradability requirements as stipulated in EN 17033 are likely to actually biodegrade to CO_2 and water (and biomass) at sufficient rate when applied in agri- or horticulture in the Netherlands. Certification according to *'DIN geprüft Biodegradable in soil', 'OK Biodegradable SOIL'*, *'OK compost HOME'* and *'DIN Geprüft Home compostable'* is considered a reliable confirmation that fulfilment of the biodegradability requirements of EN 17033 has been demonstrated.

Samenvatting *(Nederlands)*

In dit rapport worden de bevindingen weergegeven van een literatuurstudie die onafhankelijk is uitgevoerd door WFBR in opdracht van NRK-V. Het doel van de deskstudie is om inzicht te geven in de informatie die beschikbaar is in de openbare en wetenschappelijke literatuur over de biologische afbreekbaarheid van bioafbreekbare mulchfolie voor gebruik in de land- en tuinbouw.

Bioafbreekbaarheid van plastic is het vermogen om biologische afbraak te ondergaan in een geschikte omgeving. Biologische afbraak (ook wel biodegradatie) is niet alleen afhankelijk van de samenstelling/chemie van het polymeer, maar ook van de aanwezigheid en activiteit van de biologische actoren die bij het proces betrokken zijn. Dit betekent dat de bioafbreekbaarheid van plastics in de bodem kan verschillen van die in industriële composteeromstandigheden.

De biodegradatie van plastic wordt gedefinieerd als het volledige microbiële gebruik ervan, resulterend in de omzetting in CO_2, (en/of CH_4), water en biomassa door de metabole activiteit van micro-organismen. Niet alle materialen die *'biologisch afbreekbaar', 'oxo-(bio)afbreekbaar'* of *'composteerbaar'* genoemd worden, zullen daadwerkelijk bij omgevingstemperaturen in de bodem voldoende snel biologisch afgebroken worden om ophoping van plastic (residuen) in het veld te voorkomen.

Mulchfolie wordt veelal geproduceerd door polymeer grondstoffen via extrusie met andere componenten zoals verwerkingshulpmiddelen, weekmakers en kleurstoffen (middels masterbatches) te combineren tot een granulaat dat vervolgens in een volgende stap tot folie wordt verwerkt. Met betrekking tot de bioafbreekbaarheid en eventuele effecten op het milieu is het belangrijk om niet alleen rekening te houden met de polymeer bestanddelen, maar met alle componenten die worden gebruikt om de mulchfolie te produceren.

In dit rapport wordt de bioafbreekbaarheid besproken van de belangrijkste polymeer bestanddelen die gewoonlijk worden gebruikt voor bioafbreekbare mulchfolie. Hieronder vallen (thermoplastisch) zetmeel en verschillende polyesters, waaronder poly(butyleenadipaat-co-tereftalaat) (PBAT), polybutyleensuccinaat (PBS), polymelkzuur (PLA) en polyhydroxyalkanoaat (PHA). Het is van belang te beseffen dat algemene uitspraken over de biologische afbreekbaarheid van deze polymeren niet mogelijk zijn, omdat variaties in comonomeersamenstelling, molaire massa, en dergelijk, binnen een polymeerfamilie aanzienlijke effecten kunnen hebben op fysische eigenschappen en biodegradatie.

Polymeren die voldoen aan de vereisten voor biodegradatie zoals bepaald in EN 17033 zullen waarschijnlijk in voldoende mate biologisch worden afgebroken tot CO_2 en water (en biomassa) wanneer ze worden toegepast in de land- of tuinbouw in Nederland. Certificering volgens *'DIN geprüft Biodegradable in soil', 'OK Biodegradable SOIL', 'OK compost HOME'* en *'DIN Geprüft Home compostable'* wordt beschouwd als een betrouwbare bevestiging dat is aangetoond dat wordt voldaan aan de vereisten voor biodegradatie in EN 17033.

1 Introduction

1.1 Background

Eric Schutjes and Rob Verhagen (representing NRK Verpakkingen) visited Christiaan Bolck and Maarten van der Zee (Wageningen Food & Biobased Research, WFBR) to discuss possibilities for WFBR to investigate and summarize information regarding biodegradable mulch film for use in agriculture and horticulture. The interest of NRK Verpakkingen (NRK-V) for this topic was raised because of the current discussion on bioplastics and the fact that there are specific questions from both government and growers, in the context of the public debate and legal developments like the Dutch 'Landelijk Afvalbeheerplan' (LAP3) [1].

Plastic mulch is widely used for more than 40 years in horticultural production to reduce weed pressure and ultimately enhance crop yields [2, 3]. Complete removal of these mulch films, originally mainly consisting of light density polyethylene (LDPE), is difficult, time consuming and expensive: thus every year a substantial amount of plastic mulch remains in the fields, is eventually fragmented through photodegradation, and ends up being incorporated into the soil system through tillage. In response to this issue, biodegradable plastic materials (e.g. starch-based polymers and polyesters) appeared on the market 20 years ago as products of short "shelf life" in the field, and by now have become a viable alternative to plastic mulch. Although biodegradable plastic mulch is designed to be degraded *in situ*, this sometimes fails to happen and it has been observed to accumulate in the field over the years [4-6]. A dedicated standard to assess their biodegradability and ecotoxicity in soil has been developed and was adopted in 2018 (EN 17033) [7]. The potential environmental benefits of using biodegradable mulch films above conventional plastics or no mulch films will only hold for materials that do not accumulate in the environment. NRK-V would like to have better insight in the biodegradability of biodegradable mulch film, and commissioned WFBR to perform an independent desk study focussing on a meta-analysis of existing literature.

1.2 Objective and scope

The objective of the desk study is to provide insight in the information available in the public and scientific literature regarding the degradability of biodegradable mulch film for use in agriculture and horticulture. Although the reason for this study is that the potential (environmental) benefits for using biodegradable mulch films will only hold for materials that do not accumulate in the environment, the study does not include a detailed search and evaluation of the literature regarding these reputed benefits (such as reduction in microplastics, less water usage, less herbicides, better hygiene, higher yields, soil quality, application in biological farming). Also out of scope is an inventory and summary of the relevant national and/or EU directives and regulations (such as LAP3, the European Strategy for Plastics in a Circular Economy, the European Commission's Waste framework directive, the EC directive on the reduction of the impact of certain plastic products on the environment, and the EC directive on fertilisers and soil improvers) and its implications regarding requirements for (biodegradable) mulch films.

This desk study report summarizes the information found in the public and scientific literature, addressing:

- Whether or not currently available biodegradable mulch films will actually biodegrade to CO_2 and water (and biomass) when applied in agri- or horticulture in the Netherlands, and the time frame in which this occurs.
- The mechanisms through which biodegradation occurs of the currently available biodegradable mulch film materials (such as starch/PBAT or PLA/PBAT blends), and what conditions are needed to make that happen.
- A brief explanation of the difference between biodegradable and bio-based, as well as the difference between biodegradable and oxo-degradable materials.

2 Defining biodegradability of polymeric materials

Before getting into the biodegradation of specific materials, some background is provided regarding how biodegradability is defined. The next sections give some guidance on the difference between biodegradable and bio-based, on what is understood by oxo-degradable materials, how biodegradation can be assessed, and relevant standards and certification.

2.1 Biodegradable *versus* biobased

The term bioplastic refers to either the bio-based origin of a plastic or to the biodegradable character of a plastic. Bio-based and biodegradable are not synonymous (Figure 1) and therefore the term bioplastic is confusing. It is more clear to specify which of the two aspects, or perhaps both, are applicable.

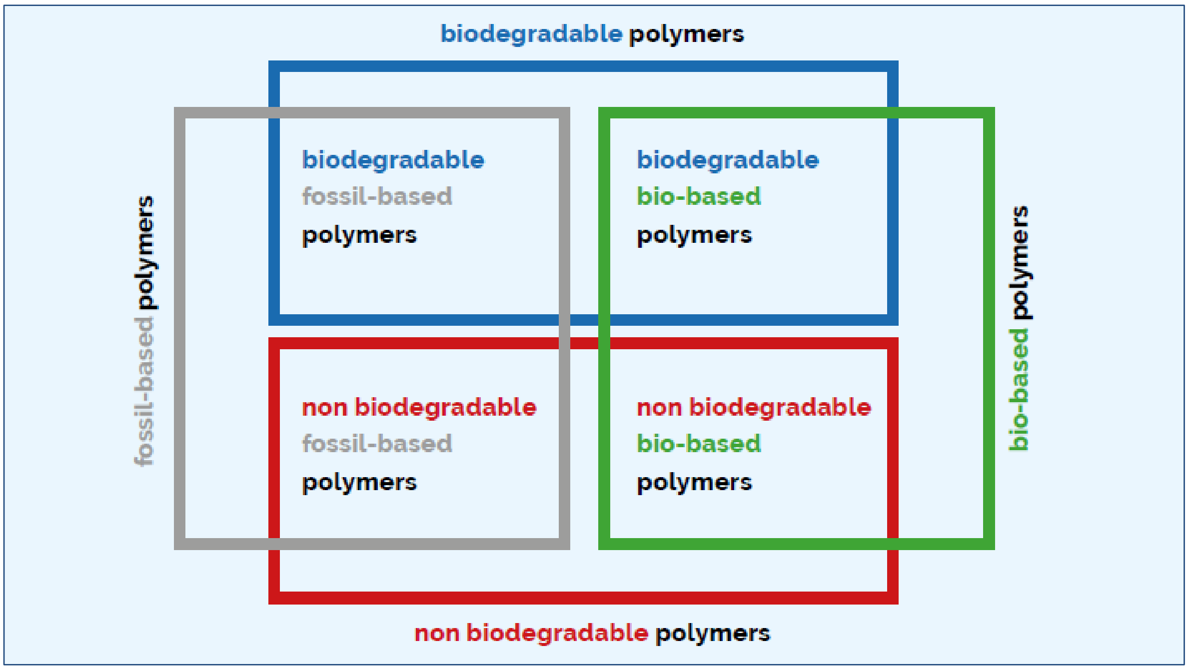


Figure 1. *Overview of the three subcategories of plastic materials that make up 'bioplastics': (i) biodegradable, fossil-based polymers (top left), (ii) biodegradable, bio-based polymers (top right), and (iii) non-biodegradable, bio-based polymers (bottom right) [8].*

'Bio-based' is defined in European standard EN 16575 [9] as 'derived from biomass'. Therefore, a bio-based product is a product wholly or partly derived from biomass. Biomass is material of biological origin, excluding material embedded in geological formations and/or fossilized [9]. Examples of biobased polymers are starch and cellulose, but also plastics such as PLA or bio-PE whose building blocks are produced from sugars. A bio-based product is normally characterized by the bio-based carbon content or the bio-based content. The bio-based carbon content in a material can be measured according to e.g. ISO 16620-2 or EN 16640 [10, 11]. The bio-based content of a material can be determined with e.g. ISO 16620-4 or EN 16785-1 [12, 13].

'Biodegradable' materials are materials that can be broken down by microorganisms (bacteria or fungi) into water, naturally occurring gases like carbon dioxide (CO_2) and methane (CH_4) and biomass (e.g. growth of the microorganism population). Biodegradation depends strongly on the environmental conditions: temperature, presence of microorganisms, presence of oxygen and water. So both the biodegradability and the degradation rate of a biodegradable plastic product may be different in the soil, on the soil, in humid or dry climate, in surface water, in marine water, or in human made systems like home composting, industrial composting or anaerobic digestion [8, 14]. How biodegradability of plastics can be assessed is discussed in section 2.3.

2.2 Biodegradable *versus* oxo-degradable

In the case of oxo-degradable plastics, additives are incorporated in conventional plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephtalate) (PET) and sometimes also poly(vinyl chloride) (PVC) at the moment of conversion into final products. The most recognized among these chemicals are so-called 'oxo' (pro-oxidant) additives. These contain metal salts (often iron, manganese, nickel and cobalt), that - upon external UV-light or thermal treatment for activation - trigger oxidation reactions involving radicals that ultimately result in breaking of the C–C backbone bonds in the polymers and, thereby, the formation of compounds of lower molecular weight. In a second phase, the resulting oxidized fragments are claimed to eventually undergo biodegradation.

Producers of pro-oxidant additives claim their products to be 'degradable', 'biodegradable', 'oxo-degradable', or 'oxo-biodegradable'. However, these additives appear to mainly facilitate fragmentation of the materials and compelling evidence suggests that oxo-degradable plastics take longer than claimed to fully biodegrade to CO_2 resulting in accumulation of very small fragments which contribute to microplastics pollution [15-20].

The European Union has recently banned the use of oxo-degradable plastics because of a lack of consistent evidence about speed of breakdown in the environment, and fears that false claims around this are misleading consumers. Directive 2019/904 came into force on 3 July 2019 and has to be transposed by the Member States by 3 July 2021 [21].

2.3 Measuring biodegradability of plastics

Biodegradability of plastic describes the potential to undergo biodegradation in a suitable environment. Biodegradation does not only depend on the chemistry of the polymer, but also on the presence and activity of the biological systems involved in the process. When investigating the biodegradability of a material, the effect of the environment cannot be neglected. Microbial activity, and hence biodegradation, is influenced by:

- The presence (and activity) of micro-organisms,
- The availability of oxygen,
- The amount of available water,
- The temperature,
- The chemical environment (pH, electrolytes and so on).

Numerous ways for the experimental assessment of polymer biodegradability have been described in the scientific literature [22]. Because of slightly different definitions or interpretations of the term 'biodegradability', the different approaches are therefore not equivalent in terms of information they provide or the practical significance.

Presently, the biodegradation of plastic is defined as its complete microbial metabolic utilisation, resulting in its conversion to CO_2, CH_4 and biomass by the metabolic activity of microorganisms [8, 14, 23]. Scientifically, the correct way of applying a direct assessment for the biodegradation of a material is to trace all organic constituents, from the test material (input) to its end products (output). For plastics that mainly consist of carbon-based polymers and additives, it is desirable to follow biodegradation according to:

$$C_{\text{polymer}} \rightarrow CO_2\ (+\ CH_4) + C_{\text{biomass}} + C_{\text{residual polymer}}$$

Technically, this can be done by labelling the test material with stable (^{13}C) or radioactive (^{14}C) isotopes and following the labelled carbon through the biodegradation process until completion in a closed system [24-26]. This direct test method, however, is technically complex and expensive, and therefore neither well suited nor feasible for a general testing scheme.

A practical simplified approach to assess ‘biodegradability’ typically is conducted in (standard) laboratory tests in small (0.1 – 4 L) closed vessels under controlled conditions favourable for biodegradation. These tests are coupled to a respirometric analysis of the amount of the evolved gas(es) CO_2 (and/or CH_4). Techniques to measure the gas evolution may differ, but the amount of end product evolved over time serves as a proxy for the extent of biodegradation. It is important to understand that tests are carried out with biological systems and that these are never identical, and that heterogeneity must therefore be taken into account. Tests typically stipulate a conversion extent of 90%, either absolute or relative to the reference material (usually cellulose = positive control) and/or reaching the plateau phase. This does not mean that 10% residual (micro)plastics is tolerated, but merely accounts for the fact that some polymeric carbon is used by microorganisms for new biomass formation (growth).

Although (visual) disintegration or weight loss is sometimes used as a screening parameter to assess the degradation of plastic mulching film in its field of application, it cannot be used to prove its complete microbial metabolic utilisation. When a mulching film for example is composed of a blended compound or copolymers, complete disintegration can be achieved by the biodegradation of one of the components whereas other components could persist in the soil with possible harm for the environment [27, 28].

2.4 Standards and certification

Standards and certification are a tool to formally confirm a certain procedure or the accuracy of a claim. A **standard** is usually a formal document that establishes uniform technical methods, processes, practices and/or criteria. **Certification** is the formal attestation or confirmation of certain characteristics of a product, person, or organization. This confirmation is often, but not always, provided by some form of external review, assessment, or audit.

2.4.1 Standards

Standard test methods for biodegradable plastics were beginning to be developed in the early 1990s, first on a regional level by the American Society for Testing and Materials (ASTM) and the European Committee for Standardization (CEN), later followed by the International Organization for Standardization (ISO) to adopt test methods on a global level [29]. The currently existing laboratory standards for plastic biodegradation in **soil** are listed in Table 1.

Table 1. Current standards for the assessment of the biodegradability of plastics in soil.

Standard No.	Title	Current version
Standards for plastics		
EN-ISO 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	2019 [30]
ASTM D5988	Standard test method for determining aerobic biodegradation of plastic materials in soil	2018 [31]
Other standards		
EN-ISO 11266	Soil quality - Guidance on laboratory testing for biodegradation of organic chemicals in soil under aerobic conditions	2020 [32]
EN-ISO 14239	Soil quality - Laboratory incubation systems for measuring the mineralization of organic chemicals in soil under aerobic conditions	2020 [33]
EN-ISO 15473	Soil quality - Guidance on laboratory testing for biodegradation of organic chemicals in soil under anaerobic conditions	2020 [34]
EN-ISO 16072	Soil quality - Laboratory methods for determination of microbial soil respiration	2011 [35]

In addition to standard test methods, also standards with specifications for specific products were developed. This was first done for compostable products (packaging), i.e. requirements for products designed to biodegrade in the managed environment of industrial composting facilities [36-39]. These standards stipulate that to be considered compostable, it needs to be demonstrated that:

1. The material and its relevant organic components (>1 wt.%) are fully biodegraded under composting conditions.
2. Disintegration of the material takes place in a composting process for organic waste within a specified period of time.
3. The material has no negative effect on the composting process.
4. The degradation products are environmentally safe, i.e. the quality of the final compost is not negatively influenced by the material.

For all these criteria, the standard defines test methods to be used and corresponding pass levels.

Because biodegradability shall be considered a system property, not only depending on the plastic, but also on the degradation environment, these standards are not suited to assess the ability to biodegrade in conditions other than an industrial composting facility. Therefore, additional methods have been developed to measure biodegradability in soil, home composting conditions (at ambient temperatures), and fresh water and marine environments [29]

Recently, European standard EN 17033 was adopted with requirements for biodegradable mulch films for use in agriculture and horticulture [7]. This standard requires laboratory testing of biodegradable mulching films, including specific criteria associated with these tests, for:

1. Chemical composition (in particular for regulated metals and hazardous substances).
2. Biodegradation in soil.
3. Ecotoxicity (i.e. toxic effects on plants, invertebrates, microorganisms).
4. Selected physical characteristics (e.g., thickness, tensile stress, light transmission).

In addition, the standard specifies additional miscellaneous criteria, such as proper labelling etc.

With regard to biodegradation in soil, the standard specifies the use of ISO 17556 [30] and at least 90% conversion of mulch’s carbon into CO_2 within 2 years under ambient soil conditions, i.e. 20-28°C (25°C preferred). Compared to other standardized tests such as ASTM D5988 [31], ISO 17556 is unique in its option to use a ‘standard soil’ consisting of industrial quartz sand, Kaolinite clay, natural soil, and mature compost (serving as organic carbon source) [40].

2.4.2 Certification

To our knowledge, there is currently no accredited certification and/or labelling system in place specifically for biodegradable mulch films. However, the *DIN Geprüft ‘Biodegradable in soil’* certification scheme [41] can be used to show compliance with the European standard EN 17033. Other certification systems that could be relevant for biodegradable mulch films are listed in Table 2.

Products certified according to ‘*OK Biodegradable SOIL*’, ‘*OK compost HOME*’ and ‘*DIN Geprüft Home compostable*’ can also fulfil the biodegradability requirements of EN 17033 because the same tests and pass levels are specified. It should be noted that products that are certified according to EN 13432 and/or ASTM D6400 (i.e. industrial compostable) may prove not sufficiently biodegradable under ambient soil conditions. The corresponding labels, i.e. the last 4 rows in Table 2, only have value for determining suitable end-of-life options for the treatment of mulch film recovered from the field after its service life.

Table 2. Certification schemes that could be relevant to biodegradable mulch film.

Certification scheme	Certification body	Based on standard(s)	Label
DIN geprüft 'Biodegradable in soil'	DIN Certco	EN 17033	BIODEGRADABLE IN SOIL DIN Geprüft
OK Biodegradable SOIL	TÜV Austria	ISO 17566.2 ISO 11266 ASTM D5988	SOIL OK bio-degradable TÜV AUSTRIA SOIL
DIN geprüft 'Home compostable'	DIN Certco	AS 5810 NF T 51-800	HOME COMPOSTABLE DIN Geprüft
OK compost HOME	TÜV Austria	EN 13432 (adapted test temperature)	HOME OK compost TÜV AUSTRIA HOME

The following certification schemes are used to demonstrate compostability, but are NOT sufficient to prove biodegradability under ambient soil conditions. To be used only for determining suitable end-of-life options for the treatment of mulch film recovered from the field after its service life.

Certification scheme	Certification body	Based on standard(s)	Label
DIN geprüft 'Industrial compostable'	DIN Certco	EN 13432 EN 14995, ISO 17088 ISO 18606, AS 4736	INDUSTRIAL COMPOSTABLE DIN Geprüft
OK Compost INDUSTRIAL	TÜV Austria	EN 13432	OK compost TÜV AUSTRIA INDUSTRIAL
Compostable (European Bioplastics)	TÜV Austria DIN Certco	EN 13432	® compostable
Compostable (Biodegradable Products Institute, BPI)	DIN Certco	ASTM D6400	BPI ® COMPOSTABLE IN INDUSTRIAL FACILITIES Check locally, as these do not exist in many communities. Not suitable for backyard composting. CERT # SAMPLE

3 Biodegradability of plastics used for mulch film

3.1 Polymeric constituents of biodegradable mulch film

Plastic films are processed by extrusion, which starts with melting of pellets (resins) of a thermoplastic polymer till they become pliable. The major components of the pellets are polymeric constituents but they commonly contain several additional minor components, such as stabilisers, plasticizers and processing aids. Typically, mulch films are prepared by a local manufacturer, often referred to as a “converter”, who will purchase polymeric feedstocks from plastics manufacturers, and blend the polymers with additional components (via master batches), such as specific processing aids, fillers, plasticizers and colorants, and then perform the film extrusion and processing [42]. Regarding biodegradability and environmental fate it is necessary to consider not only the polymeric constituents, but all components that are used to produce the mulch film, i.e. on a product level.

There are many commercially available polymers employed in biodegradable mulch film. Some examples of trade names of these polymers and polymer blends are listed in Table 3. Also within trademarks there is a variety of grades targeting different applications which, in tailoring desired physical properties, may vary in composition of polymer constituents, molar mass of the polymers, type and amount of additives, etc. The additives that are used in producing biodegradable mulch film are out of scope of this report. Here we will only discuss the biodegradability of the main polymeric constituents, such as starch and several polyesters, including poly(butylene adipate-co-terephthalate) (PBAT), poly(butylene succinate) (PBS), poly(lactic acid) (PLA) and poly(hydroxy alkanoate) (PHA). Their chemical structures are shown in Figure 2.

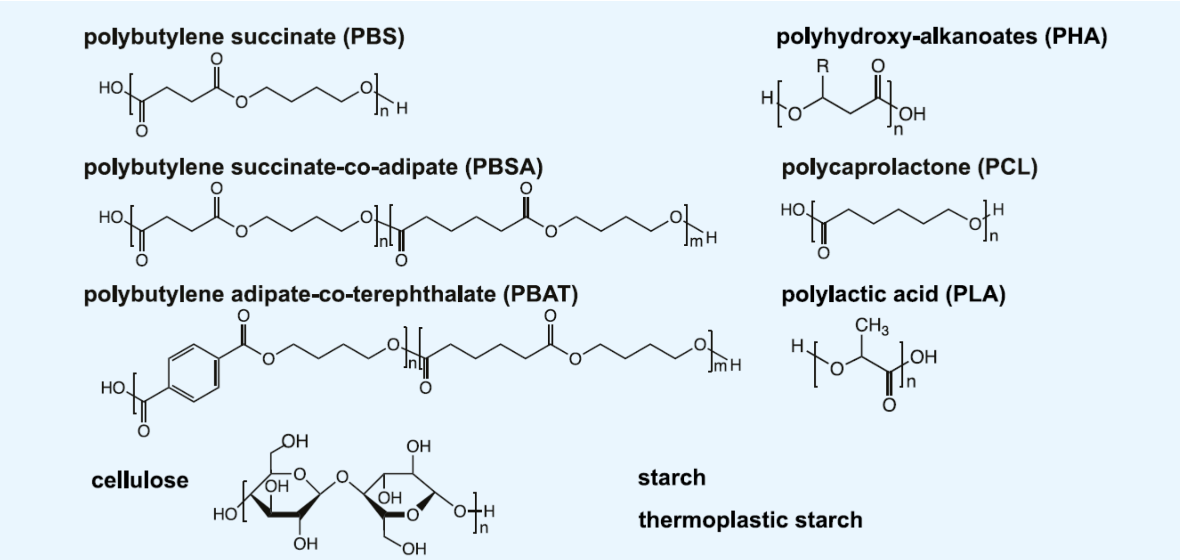


Figure 2. *Overview of commonly used biodegradable polymers with their chemical structures [8].*

Table 3. Examples of commercially available polymers employed in biodegradable mulch film (adapted from [42-45]).

Product name	Producer	Polymeric constituents	Remarks
Biocycle	PHB Industrial	Blends of poly(hydroxy alkanoate)	Various PHB grades from sugarcane
Bio-Flex	FKUR	Poly(lactic acid) co-polyester blend	A variety of compounds based on various biodegradable polyesters including a series of films that are certified home compostable
Biolice	Limagrain	Poly(butylene adipate-co-terephthalate) cereal flour blend	Various grades, certified compostable (EN 13432)
Biomax TPS	DuPont/Plantic	Thermoplastic starch blend	Various Plantic starch based compounds. DuPont only refers to injection molding grades and not film grades
Biomer	Biomer	Poly(hydroxy alkanoate)	Various PHB grades, certified soil degradable
Biopar	United Biopolymers	Thermoplastic starch blend with (co)polyesters	Various film grades, certified compostable (EN 13432)
BioPBS(A)	PTTMCC	Poly(butylene succinate) or poly(butylene succinate-co-adipate)	Various PBS and PBSA grades, PBSA is certified soil biodegradable
Biocosafe	Xinfu	Thermoplastic starch blend with PBAT, PBS and/or PBSA	Various grades, certified compostable
DaniMer	Danimer	Poly(hydroxy alkanoate)	Certified soil biodegradable grades (ASTM 5988)
Ecoflex	BASF	Poly(butylene adipate-co-terephthalate)	Various grades, some certified soil biodegradable
Ecovio	BASF	Blend of Poly(butylene adipate-co-terephthalate) with poly(lactic acid)	Various grades. One specific grade is certified as soil biodegradable (EN 17033)
EnPol	IRe	Poly(butylene succinate) and poly(butylene adipate-co-terephthalate)	PBAT grades are certified soil biodegradable
GreenBio	Tianjin	Poly(hydroxy alkanoate)	Various PHA grades
Ingeo	NatureWorks	Poly(lactic acid)	Various PLA grades, certified compostable (EN 13432), in mulch films used in some blends
MaterBi	Novamont	Thermoplastic starch blend with various (co)polyesters	Various grades, some used for biodegradable mulching film certified according to EN 17033
Meredian	Meridian	Poly(hydroxy alkanoate)	Old name, is now Danimer (see above)
Mirel	Metabolic	Poly(hydroxy alkanoate)	Mentioned in literature, but does not exist anymore
Naturecycle	Custom Bioplastics	Thermoplastic starch blend with various (co)polyesters	Mentioned in literature, but does not exist anymore
Paragon		Thermoplastic starch	Mentioned in literature, but no film grades; just injection moulding grades for petfood
ReNew		Poly(hydroxy alkanoate)	Old brand name, is now Danimer (see above)
SoGreen	Tianjin	Poly(hydroxy alkanoate)	Tradename of Tianjin GreenBio (see above)
Succinity	Succinity	Poly(butylene succinate)	Mentioned in literature, but in fact producer of succinic acid monomer (no polymers)

3.2 Thermoplastic starch (TPS)

Starch, being an abundantly available natural glucose based polymer, is generally considered as readily biodegradable in a wide variety of natural environments, including soil. It is a carbon and energy source for many microorganisms in both aquatic and terrestrial environments. Also when processed into thermoplastic starch, the starch molecules are rapidly metabolized and converted to CO_2 in respirometric biodegradation tests [46, 47]. The rapid biodegradation of a range of thermoplastic starch materials containing various mineral fillers was recently confirmed by Julinová *et al* using respirometric methods in aerobic and anaerobic aqueous environments and in soil [48]

In the first attempts to produce biodegradable films, granular starch was blended in low percentages (6-7% by weight) into polyethylene film [49]. In 1977, the first mixtures were made using plasticized starch in PE [50]. Although these materials disintegrated in the soil, it became clear that this was due to the fact that the starch was biodegraded and left the PE matrix weakened [51, 52]. After the fragmentation of the material, small non-degradable plastic residues are obtained and accumulated, thus making their disposal even more difficult [52]. These materials are currently generally considered as unsuitable for mulch applications, but occasionally they can still be found on the market. They, however, will not fulfill the biodegradability criteria in EN 17033.

Thermoplastic starch as such lacks the physical properties needed for the functional use of mulch films. It is therefore usually blended with other polymers to improve properties such as toughness, flexibility, strength, tear resistance, durability, etc. Most biodegradable TPS materials therefore contain, besides starch, also polyesters such as PCL, PBAT, PBS, PBA, PBSe, PLA and PHA. Many material and film producers employ their own specific blends of polymers. When used as filler, degradation of the starch can enhance the physical disintegration of the material. More aspects regarding the biodegradation of polymer blends are discussed in section 3.4.

3.3 Polyesters

3.3.1 PBAT - poly(butylene adipate-co-terephthalate)

PBAT is probably the most commonly used polymer to produce biodegradable mulch film, due to its favourable mechanical properties for this application. However, it should be noted that PBAT is a generic name for a polymer containing both butylene adipate (BA) and butylene terephthalate (BT) units. The ratio between BA and BT units can vary, as well as their distribution within the polymer chains, the molar mass of the polymer, etc. which all will have effect on properties, including the biodegradation rate. Nevertheless, there are several grades (from different producers) that have been certified to be ‘soil biodegradable’ or ‘home compostable’ (see section 2.4.2), implying that was demonstrated that sufficient conversion of the polymer to CO_2 was reached in ambient (soil) conditions within the specified test period [53, 54].

PBAT is also probably one of the best studied polymers with regard to its biodegradability in the soil environment. Several studies provided indirect indications for PBAT biodegradation in soils based on determining PBAT mass loss and changes in its physicochemical properties [55-58]. More importantly, Zumstein et al. reported a novel workflow using stable carbon isotope-labeled PBAT to directly and unequivocally demonstrate its biodegradation in soil [26]. The use of ^{13}C-labeled polymers allowed them to distinguish polymer-derived CO_2 from CO_2 formed by soil organic matter mineralization. The authors studied three PBAT variants that had similar physicochemical properties and comparable total ^{13}C contents, but varied in the monomer that contained the ^{13}C-label [that is, butanediol (P*BAT), adipate (PB*AT), or terephthalate (PBA*T)]. Soil incubation of all PBAT variants resulted in $^{13}CO_2$ formation, demonstrating that soil microorganisms used carbon from all three monomer units in PBAT to gain energy. The adipate units were mineralized somewhat faster than the other two monomer units [26]. This is consistent with the decrease in the adipate-to-terephthalate ratio during soil incubation as reported for unlabeled PBAT [55]. After incubation, polymer film surfaces were imaged using scanning electron microscopy (SEM) and the incorporation of polymer-derived ^{13}C into the biomass of film colonizing microorganisms was demonstrated using element-specific, isotope-selective nanoscale secondary ion mass spectrometry (NanoSIMS). With this technique it was demonstrated that polymeric carbon was not only mineralized to CO_2, but was also incorporated in microbial biomass. From the assessment of all the key steps involved in the biodegradation process of PBAT (i.e. microbial polymer colonization, enzymatic depolymerization on the polymer surface, and microbial uptake and utilization of the released low–molecular weight compounds), it was concluded that the depolymerization step controlled the rate at which PBAT is mineralized in soils [26], which is consistent with the findings reported earlier by Müller *et al.* [59].

These detailed studies confirm that the investigated PBAT grade is fully biodegraded in the soil environment (complete microbial metabolic utilization, see section 2.3). Furthermore, the results justify the requirement of 90% carbon conversion to CO_2 to demonstrate complete biodegradation (see section 2.4.1) because in the biodegradation process a part of the polymeric carbon is indeed incorporated by microorganisms for new biomass formation (growth).

3.3.2 PBS, PBA and PBSA - poly(butylene succinate), poly(butylene adipate) and their copolymer poly(butylene succinate-*co*-butylene adipate)

PBS is the copolymer of butanediol and succinic acid. It is a aliphatic semi-crystalline polyester. The PBS polymer backbone is flexible and contains readily hydrolysable ester bonds, which are prone to catalytic degradation by microorganisms or enzymes. Microorganisms can secrete the corresponding enzymes that catalyze the hydrolysis of PBS [60]. The degradation of PBS, PBA and their copolymer poly(butylene succinate-co-butylene adipate) (PBSA) have been a subject of several studies, with a lot of emphasis on systematic studies with hydrolytic enzymes [61-73]. It was shown already in the 1970s that PBS, PBA and many related polymers are enzymatically hydrolyzed by lipases excreted by fungi, e.g. from *Rhizopus delemar* [74]. The enzymatic hydrolysis rate is influenced by both chemical structure of the polymer and degree of crystallinity [64, 67]. Degradation tests of ^{14}C labeled poly(butylene adipate) showed that microorganisms are able to further degrade oligomers formed during the hydrolysis of PBA [62]. Furthermore, microorganisms capable of degrading BPS and PBSA have been isolated from soil and characterized [75, 76]

Although disintegration of PBS (and copolymers) in soil has been reported [77-82], we could find only few studies that have assessed the biodegradation of PBS in soil with respirometric tests showing complete conversion to CO_2. Narancic *et al* [83] included one PBS grade in an extensive study assessing the biodegradability of a range of biodegradable polymers (and compounded combinations) in a range of standard test conditions. They reported sufficient biodegradation under industrial composting conditions, but slow conversion to CO_2 (and/or CH_4) at ambient conditions where this material failed to pass the biodegradation criteria of ISO and ASTM standards in soil, home composting, anaerobic digestion, and aquatic conditions [83]. Nevertheless, there are some other PBS grades that have been certified to be ‘soil biodegradable’ or ‘home compostable’ (see section 2.4.2), implying that was demonstrated that sufficient conversion of the polymer to CO_2 was reached in ambient (soil) conditions within the specified test period [53, 54]. Those grades often contain also some butylene adipate moieties (i.e. PBSA) which is in line with the general findings that biodegradation rate of PBS(A) increases with increasing adipate-to-succinate ratio[68, 75].

3.3.3 PLA - poly(lactic acid) - polylactide

PLA is known for its excellent compostability at elevated temperatures in industrial composting facilities and there are many PLA grades and products based upon them certified “industrial compostable” (see section 2.4.2) [84, 85]. However, in natural environments at ambient conditions, i.e. below 25°C, PLA is not rapidly degraded. For example, Itävaara *et al* studied biodegradation of PLA at different elevated temperatures in both aerobic and anaerobic, aquatic and solid state conditions [86]. In an aerobic aquatic headspace test the mineralization of PLLA was very slow at room temperature, but faster under thermophilic conditions. Table 4 shows the length of time required to degrade PLA (in water) at different temperatures as reported by Lunt [87].

Table 4. Temperature dependence of hydrolysis and biodegradation of PLA in water [87].

Temperature	Onset of fragmentation	Onset of biodegradation
4°C	64 months	123 months
13°C	25 months	48 months
25°C	6 months	11.4 months
30°C	4.4 months	8.5 months
50°C	1.5 months	2.9 months
60°C	8.5 days	16 days
70°C	1.8 days	3.5 days

The higher temperatures in industrial composting enhance the hydrolysis of PLA, which is the initial mechanism to reduce PLA molecular weight before available microorganism can consume the low molecular weight PLA. At elevated temperatures, i.e. higher than PLA's glass transition temperature (T_g≈58°C), the mobility of PLA molecules is increased, which plays a major role in its degradation since the increased flexibility of polymer chains leads to microstructural changes, enhances the rate of hydrolysis, and increases the polymer hydrophilicity due to sorption of water into the polymer matrix [86, 88-90]. At these elevated temperatures, PLA degradation starts through hydrolysis with no enzymatic involvement and low molecular weight oligomers are formed. If these oligomers are sufficiently small, they become soluble in water and can be digested by microorganisms. According to Lunt, a molar mass of 10,000 Dalton (as determined by GPC in reference to polystyrene standards), is sufficiently small to allow biodegradation at ambient conditions [87]. Other studies suggest that the molar mass should be even lower (<2,500 Da) to allow biodegradation in aqueous environments [91]. We could not find further literature data showing at what molar mass PLA becomes readily biodegradable in ambient soil conditions.

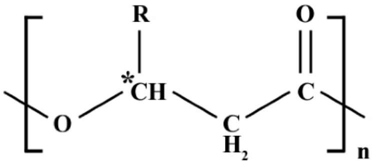
Some papers report the isolation of microorganisms from compost (bacteria, fungi or actinomycetes) capable of degrading PLA at ambient conditions [92-94]. However, that these microorganism can be found does not imply that they are sufficiently active in practical field situations to ensure that PLA does not accumulate when applied in mulch film.

Although there are limited reports about the biodegradation of PLA in soil, few researchers have focused on using bio-augmentation strategies for both fungal as well as bacterial strains to enhance the rate of degradation of PLA in natural soil environment [92, 95-97]. Satti *et al.* evaluated the biodegradation of PLA film in a soil matrix under mesophilic conditions using natural attenuation, bio-augmentation and bio-stimulation [92]. The rate of mineralization of the PLA was found to be very slow as 10% in soil at 150 days and there was no evidence of abiotic degradation of the polymer at 30°C. Bioaugmentation with previously isolated PLA-degrading bacteria (*Sphingobacterium sp.* strain S2 and *Pseudomonas aeruginosa* strain S3) and stimulating the native microbial community with 0.2% sodium lactate significantly enhanced the mineralization rate of PLA to 22 and 24%, respectively at 150 days (with no adverse effect on soil health as well as its nitrification potential). The authors conclude that bio-stimulation and bio-augmentation can be considered as potential routes to enhance the degradation of PLA at ambient temperature [92].

By itself, PLA is not particularly suitable for (mulch) film applications because it is too stiff. In recent years, a lot of additives and masterbatches have been developed that can be added to improve specific properties of PLA. Examples are impact modifiers improving the impact resistance, and chain extenders that increase the melt strength. Properties are also modified/improved by blending PLA with other polymers [98]. On the other hand, PLA is often added to formulations for films, in particular to make them stronger and cheaper, and in the case of fossil based formulations, to increase the biobased content. For biodegradable applications it is important to consider the effect additives and blended polymers may have on the biodegradation rate of the final product. In some cases blending with rapidly biodegrading polymers is used to tailor the disintegration rate of PLA-blends, in particular with regard to biodegradation in ambient conditions. A common biodegradable PLA blend is the one with PBAT (see section 3.3.1) which results in material properties that are widely applicable in film type products. PLA blends with starch, PBS and PHA are also applied (see section 3.4).

3.3.4 PHA - poly(hydroxy alkanoate)

PHAs are a family of linear polyesters, specifically poly(3-hydroxy alkanoate)s, that are produced by microorganisms [99, 100]. The general chemical structure of the PHA family is shown in Figure 3 [101]. PHA polymers can be synthesized by a wide variety of bacteria through the fermentation of sugars, lipids, alkanes, alkenes and alkanoic acids. In the presence of an abundant carbon source when other essential nutrients such as oxygen, phosphorous or nitrogen are limited, many microorganisms usually assimilate and store PHA for future consumption. Once extracted from the bacterial cells, PHA exhibit thermoplastic and elastomeric properties. The most well-known among them is the thermoplastic poly(R-3-hydroxybutyate), also referred to as PHB [99].



Poly(3-hydroxyalkanoate)

R group	Carbon no.	PHA polymer
methyl	C_4	Poly(3-hydroxybutyrate)
ethyl	C_5	Poly(3-hydroxyvalerate)
propyl	C_6	Poly(3-hydroxyhexanoate)
butyl	C_7	Poly(3-hydroxyheptanoate)
pentyl	C_8	Poly(3-hydroxyoctanoate)
hexyl	C_9	Poly(3-hydroxynonanoate)
heptyl	C_{10}	Poly(3-hydroxydecanoate)
octyl	C_{11}	Poly(3-hydroxyundecanoate)
nonyl	C_{12}	Poly(3-hydroxydodecanoate)
decyl	C_{13}	Poly(3-hydroxytridecanoate)
undecyl	C_{14}	Poly(3-hydroxytetradecanoate)
dodecyl	C_{15}	Poly(3-hydroxypentadecanoate)
tridecyl	C_{16}	Poly(3-hydroxyhexadecanoate)

Figure 3. General structural formula of poly(3-hydroxy alkanoate) and list of various family members [101].

A remarkable characteristic of PHAs is their biodegradability in various environments where a considerable number of microorganisms excrete PHA depolymerases to hydrolyze solid PHA into water-soluble oligomers and monomers, which are also utilized as nutrients for their own cells [102]. PHA is degraded in various environments such as soil, sewage, sea water, and lakes [8]. As mentioned earlier, biodegradation depends on several factors such as microbial activity in the environment, humidity, temperature, pH, and molecular weight of the polymer. The most important factors related to the PHA characteristics which influence its degradation are (i) stereospecificity, since only monomers in configuration (R) are hydrolyzed by depolymerases; (ii) crystallinity, since the degradation decreases with higher crystallinity; (iii) molecular weight, because the polymers of low molecular weight are generally degraded more rapidly than those with high molecular weight; and (iv) monomeric composition of PHA [100, 102-106].

The most important commercially available PHA's are poly(3-hydroxy butyrate) (PHB), poly(3-hydroxy butyrate-*co*-4-hydroxy butyrate) (P3HB4HB), poly(3-hydroxy butyrate-*co*-3-hydroxy valerate (PHBV), and poly(3-hydroxy butyrate-*co*-3-hydroxy hexanoate) (PHBH). PHB is a highly crystalline thermoplastic material that is more stiff than PP. However, it is very brittle which limits its applicability in film type products. PHBV is more tough and its stiffness is slightly higher than PP. It has a strain at break of 10-50%. P3HB4HB and PHBH have mechanical properties (a.o. strain at break) that are comparable to those of PP and HDPE [98]. Most currently available PHAs have been certified to be 'soil biodegradable' or 'home compostable' (see section 2.4.2), implying that was demonstrated that sufficient conversion of the polymer to CO_2 was reached in ambient (soil) conditions within the specified test period [53, 54]. The range of commercially available PHA-grades is increasing and also product development and blending PHAs with other biodegradable polymers leads to a family of compounds with a broad range of physical properties and biodegradability.

3.4 Blends/compounds

Predicting the degradation behavior of a polymer blend on the basis of the properties of pure components is, as a rule, very difficult. Indeed, the blend composition, as well as the possible presence of a compatibilizer, can strongly affect the degradation behavior of a polymer blend and can differ from the degradation routes of the pure components since interactions among the different species in the blends during degradation and among the degradation products can occur. Therefore, the additive rule cannot be often applied in case of degradation of polymer blends, since the degradation rate of a polymer blend can result to be higher, intermediate or lower than that of the pure components [107].

Many reports can be found of blending and compounding combinations of the biodegradable polymers we discussed in the earlier sections 3.2 and 3.3 and the corresponding characterization and evaluation of resulting materials. In case soil biodegradability data of these blends are presented, these often just involve the assessment of disintegration and or weight loss during soil exposure [28, 57, 79, 80, 108-114]. However, showing that the disintegration rate of, for example, a PLA material increases by blending it with another biodegradable polymer such as starch, does not prove that the complete microbial metabolic utilization of the PLA fraction (resulting in its conversion to CO_2) is accelerated or actually takes place at all.

We could find only limited reliable studies that have assessed the biodegradation of blends in soil with respirometric tests showing the conversion of polymeric carbon to CO_2. Narancic *et al* assessed the biodegradability of a range of biodegradable polymers (and compounded combinations) in a set of standard test conditions, including soil and home composting at ambient temperatures [83]. They included the following blends (in which: PCL = polycaprolactone; PHO = poly(hydroxy octanoate):

- PLA/PCL (80/20)
- PLA/PBS (80/20)
- PLA/PHB (80/20)
- PLA/PHO (85/15)
- PHB/PHO (85/15)
- PCL/PHO (85/15)
- PCL/TPS (70/30)
- PHB/PCL (60/40)
- PHB/PBS (50/50)

The biodegradation of these blends in home composting conditions was assessed with ISO 14855 (adapted for lower composting temperature, i.e. 28°C) and biodegradation in soil was assessed with ISO 17556. In these cases, the biodegradation curves were consistent with the mineralization of the continuous phase polymer. For the PLA compounds this means that the biodegradation of the PLA fraction was not enhanced by the addition of e.g. PHB [83].

4 Impact of agricultural weathering

In practice, biodegradation of mulch film cannot be considered completely separate from agricultural weathering. Exposure to the environment can lead to significant physicochemical changes in the structure of biodegradable materials which either enhance or slow down the biodegradation. Sunlight, particularly its UV component, is the most significant factor. Once the canopy of a plant is formed to block solar radiation exposure from the biodegradable materials, the effect is reduced. It has been reported that polymers such as PLA and PBAT undergo photochemical reactions such as Norrish Type I and II reactions shown in Figure 4 [42, 56, 115].

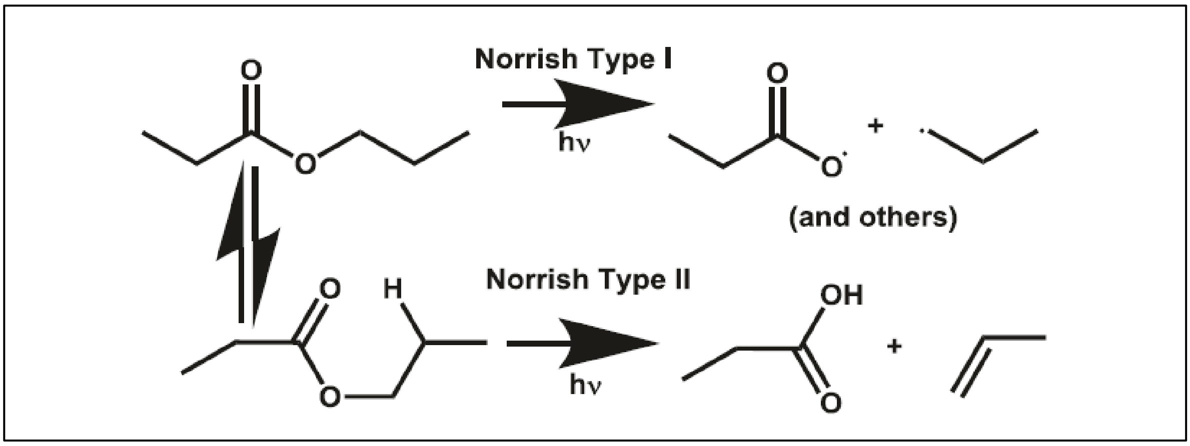


Figure 4. Norrish type I and type II photochemical reactions[42].

Norrish type I reactions involves the formation of free radicals, and can lead to cross-linking, which can reduce the biodegradability of the plastic [116, 117]. It is known that colorants, particularly TiO_2 (white), enhance the Norrish Type I reaction [116]. Norrish Type II reaction entails chain scission, thus leading to depolymerization, which can enhance biodegradation [118]. In addition, due to the presence of moisture and warming from sunlight, hydrolysis of ester bonds can also occur [42].

5 Concluding remarks

Biodegradability of plastic describes the potential to undergo biodegradation in a suitable environment. Biodegradation does not only depend on the chemistry of the polymer, but also on the presence and activity of the biological systems involved in the process. This means that biodegradability in soil can be different from biodegradability in industrial composting conditions.

The biodegradation of plastic is defined as its complete microbial utilization, resulting in its conversion to CO_2, (and/or CH_4), water and biomass by the metabolic activity of microorganisms. Not all materials labelled *'biodegradable', 'oxo-(bio)degradable'* or *'compostable'* will actually biodegrade at sufficient rate at ambient temperatures in soil to prevent accumulation of plastic (residues) in the field.

Typically, mulch films are produced by combining polymeric feedstocks with other components (via master batches), such as processing aids, plasticizers and colorants, which are then further processed through extrusion into film. Regarding biodegradability and environmental fate it is important to consider not only the polymeric constituents, but all components that are used to produce the mulch film.

We discussed the biodegradability of the main polymeric constituents commonly employed for biodegradable mulch film. These include (thermoplastic) starch and several polyesters, including poly(butylene adipate-co-terephthalate) (PBAT), poly(butylene succinate) (PBS), poly(lactic acid) (PLA) and poly(hydroxy alkanoate) (PHA). It is important to realize that general statements regarding the biodegradability of these polymers are not possible, because variations of comonomer composition, molar mass, etc. within a polymer family, can have substantial effects on physical properties and biodegradation behaviour.

Polymer grades that have passed the biodegradability requirements as stipulated in EN 17033 are likely to actually biodegrade to CO_2 and water (and biomass) at sufficient rate when applied in agri- or horticulture in the Netherlands. Certification according to *'DIN geprüft Biodegradable in soil', 'OK Biodegradable SOIL'*, '*OK compost HOME*' and '*DIN Geprüft Home compostable*' is considered a reliable confirmation that fulfilment of the biodegradability requirements of EN 17033 has been demonstrated.

Literature

1. LAP3, *Derde Landelijk Afvalbeheerplan*. 2020, Ministerie van Infrastructuur en Waterstaat: https://lap3.nl/.
2. Kasirajan, S. and M. Ngouajio, *Polyethylene and biodegradable mulches for agricultural applications: A review.* Agronomy for Sustainable Development, 2012. **32**(2): p. 501-529.
3. Steinmetz, Z., et al., *Plastic mulching in agriculture. Trading short-term agronomic benefits for long-term soil degradation?* Science of the Total Environment, 2016. **550**: p. 690-705.
4. Qi, Y., et al., *Impact of plastic mulch film debris on soil physicochemical and hydrological properties.* Environmental Pollution, 2020. **266**.
5. Brodhagen, M., et al., *Policy considerations for limiting unintended residual plastic in agricultural soils.* Environmental Science and Policy, 2017. **69**: p. 81-84.
6. Thompson, A.A., et al., *Degradation Rate of Bio-based Agricultural Mulch is Influenced by Mulch Composition and Biostimulant Application.* Journal of Polymers and the Environment, 2019. **27**(3): p. 498-509.
7. EN 17033, *Plastics - Biodegradable mulch films for use in agriculture and horticulture - Requirements and test methods*. 2018, European Standard EN 17033:2018, European Committee for Standardization (CEN): Brussels.
8. SAPEA, *Biodegradability of Plastics in the Open Environment*. 2020, Science Advice for Policy by European Academies (SAPEA): Berlin.
9. EN 16575, *Bio-based products - Vocabulary*. 2014, European Standard EN 16575:2014, European Committee for Standardization (CEN): Brussels.
10. ISO 16620-2, *Plastics - Biobased content - Part 2: Determination of biobased carbon content*. 2015, International Standard ISO 16620-2:2015, the International Organization for Standardization (ISO): Geneva.
11. EN 16640, *Bio-based products - Bio-based carbon content - Determination of the bio-based carbon content using the radiocarbon method*. 2017, European Standard EN 16640:2017, European Committee for Standardization (CEN): Brussels.
12. ISO 16620-4, *Plastics - Biobased content - Part 4: Determination of biobased mass content*. 2016, International Standard ISO 16620-4:2016, the International Organization for Standardization (ISO): Geneva.
13. EN 16785-1, *Bio-based products - Bio-based content - Part 1: Determination of the bio-based content using the radiocarbon analysis and elemental analysis*. 2016, European Standard EN 16785-1:2016, European Committee for Standardization (CEN): Brussels.
14. Van Der Zee, M., *Methods for evaluating the biodegradability of environmentally degradable polymers*, in *Handbook of Biodegradable Polymers*. 2020, De Gruyter: Berlin. p. 1-21.
15. Selke, S., et al., *Evaluation of biodegradation-promoting additives for plastics.* Environmental Science and Technology, 2015. **49**(6): p. 3769-3777.
16. Deconinck, S. and B. De Wilde, *Benefits and chalanges of bio- and oxo-degradable plastics - A comparative study*. 2013, Organic Waste Stystems (OWS) Final report, Study DSL-1, Rev. 04.
17. European Commission, *Report from the Commission to the European Parliament and the Council on the impact of the use of oxo-degradable plastic, including oxo-degradable plastic carrier bags, on the environment*. 2018, European Commission, COM(2018)35 final: Brussels.
18. Kubowicz, S. and A.M. Booth, *Biodegradability of Plastics: Challenges and Misconceptions.* Environmental Science and Technology, 2017. **51**(21): p. 12058-12060.
19. Markowicz, F. and A. Szymańska-Pulikowska, *Analysis of the possibility of environmental pollution by composted biodegradable and oxobiodegradable plastics.* Geosciences (Switzerland), 2019. **9**(11).
20. Napper, I.E. and R.C. Thompson, *Environmental Deterioration of Biodegradable, Oxo-biodegradable, Compostable, and Conventional Plastic Carrier Bags in the Sea, Soil, and Open-Air over a 3-Year Period.* Environmental Science and Technology, 2019. **53**(9): p. 4775-4783.
21. European Commission, *Directive (EU) 2019/904 of the European Parliament and of the Council of 5 June 2019 on the reduction of the impact of certain plastic products on the environment*. 2019, OJ L155/1, 12.6.2019: Brussels.
22. Van Der Zee, M., *Analytical Methods for Monitoring Biodegradation Processes of Environmentally Degradable Polymers*, in *Handbook of Biodegradable Polymers: Isolation, Synthesis, Characterization and Applications*. 2011. p. 263-281.
23. Degli Innocenti, F. and T. Breton, *Intrinsic Biodegradability of Plastics and Ecological Risk in the Case of Leakage.* ACS Sustainable Chemistry and Engineering, 2020. **8**(25): p. 9239-9249.

24. Li, T., et al., *Simultaneous analysis of microbial identity and function using NanoSIMS.* Environmental Microbiology, 2008. **10**(3): p. 580-588.
25. Musat, N., et al., *A single-cell view on the ecophysiology of anaerobic phototrophic bacteria.* Proceedings of the National Academy of Sciences of the United States of America, 2008. **105**(46): p. 17861-17866.
26. Zumstein, M.T., et al., *Biodegradation of synthetic polymers in soils: Tracking carbon into CO2 and microbial biomass.* Science Advances, 2018. **4**(7).
27. Djellali, S., N. Benmahmoud, and T. Sadoun, *Biodegradation of low density polyethylene/starch films exposed to soil burial.* Annales de Chimie: Science des Materiaux, 2009. **34**(1): p. 41-48.
28. Nakashima, T., H. Ito, and M. Matsuo, *Biodegradation of high-strength and high-modulus PE-starch composite films buried in several kinds of soils.* Journal of Macromolecular Science - Physics, 2002. **41 B**(1): p. 85-98.
29. De Wilde, B., *International and national norms on biodegradability and certification procedures*, in *Handbook of Biodegradable Polymers*. 2020, De Gruyter: Berlin. p. 115–146.
30. ISO 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*. 2019, International Standard ISO 17556:2019, the International Organization for Standardization (ISO): Geneva.
31. ASTM D5988, *Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in Soil*. 2018, ASTM D5988-18, ASTM International: West Conshohocken, PA, USA.
32. ISO 11266, *Soil quality - Guidance on laboratory testing for biodegradation of organic chemicals in soil under aerobic conditions*. 2020, International Standard ISO 11266:2020, the International Organization for Standardization (ISO): Geneva.
33. ISO 14239, *Soil quality - Laboratory incubation systems for measuring the mineralization of organic chemicals in soil under aerobic conditions*. 2020, International Standard ISO 14239:2020, the International Organization for Standardization (ISO): Geneva.
34. ISO 15473, *Soil quality - Guidance on laboratory testing for biodegradation of organic chemicals in soil under anaerobic conditions*. 2020, International Standard ISO 15473:2020, the International Organization for Standardization (ISO): Geneva.
35. ISO 16072, *Soil quality - Laboratory methods for determination of microbial soil respiration*. 2011, International Standard ISO 16072:2011, the International Organization for Standardization (ISO): Geneva.
36. EN 13432, *Packaging - Requirements for packaging recoverable through composting and biodegradation -Test scheme and evaluation criteria for the final acceptance of packaging* 2000, European Standard EN 13432:2000, European Committee for Standardization (CEN): Brussels.
37. ASTM D6400, *Standard Specification for Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities*. 2019, ASTM D6400-19, ASTM International: West Conshohocken, PA, USA.
38. ISO 17088, *Specifications for compostable plastics*. 2012, International Standard ISO 17088:2012, the International Organization for Standardization (ISO): Geneva.
39. EN 14995, *Plastics - Evaluation of compostability - Test scheme and specifications*. 2007, European Standard EN 14995:2007, European Committee for Standardization (CEN): Brussels.
40. Hayes, D.J. and F.M. Flury, *Summary and Assessment of EN 17033:2018, a New Standard for Biodegradable Plastic Mulch Films*. 2018, BiodegradableMulch.org, Report No. EXT-2018-01.
41. DIN CERTCO, *Certification scheme 'Biodegradable in soil' (according to DIN EN 17033, Edition March 2018)*. 2018, DIN CERTCO, TÜV Rheinland: Berlin. p. 33.
42. Hayes, D.G., et al., *Biodegradable Plastic Mulch Films for Sustainable Specialty Crop Production*, in *Polymers for Agri-Food Applications*, T.J. Gutiérrez, Editor. 2019, Springer International Publishing: Cham. p. 183-213.
43. Guerrini, S., et al., *Agronomical Overview of Mulch Film Systems*, in *Polymers for Agri-Food Applications*, T.J. Gutiérrez, Editor. 2019, Springer International Publishing: Cham. p. 241-264.
44. Manzano, V., et al., *Mulch Plastic Systems: Recent Advances and Applications*, in *Polymers for Agri-Food Applications*, T.J. Gutiérrez, Editor. 2019, Springer International Publishing: Cham. p. 265-290.
45. Agrobiofilm, *Compostable films for Agriculture - the development of enhanced biodegradable films for melon & pepper, strawberry, vine.* 2013: Agrobiofilm Consortium, http://www.agrobiofilm.eu/temps/docs/10_13_15_25_handbook_agrobiofilm.pdf. 160.
46. van der Zee, M., et al., *Assessment of biodegradation of water insoluble polymeric materials in aerobic and anaerobic aquatic environments.* Chemosphere, 1994. **28**(10): p. 1757-1771.
47. van der Zee, M., et al., *Structure-biodegradation relationships of polymeric materials. 1. Effect of degree of oxidation on biodegradability of carbohydrate polymers.* Journal of Environmental Polymer Degradation, 1995. **3**(4): p. 235-242.

48. Julinová, M., et al., *Effect of Different Fillers on the Biodegradation Rate of Thermoplastic Starch in Water and Soil Environments.* Journal of Polymers and the Environment, 2020. **28**(2): p. 566-583.
49. Griffin, G.J.L., *Biodegradable Fillers in Thermoplastics*, in *Fillers and Reinforcements for Plastics*. 1974, AMERICAN CHEMICAL SOCIETY. p. 159-170.
50. Otey, F.H., R.P. Westhoff, and C.R. Russell, *Biodegradable Films from Starch and Ethylene-Acrylic Acid Copolymer.* Industrial and Engineering Chemistry Product Research and Development, 1977. **16**(4): p. 305-308.
51. Imam, S.H., et al., *Starch: Chemistry, microstructure, processing, and enzymatic degradation*, in *Starch-Based Polymeric Materials and Nanocomposites: Chemistry, Processing, and Applications*. 2012. p. 5-32.
52. Halley, P., et al., *Developing biodegradable mulch films from starch-based polymers.* Starch/Staerke, 2001. **53**(8): p. 362-367.
53. TÜV Austria Belgium. *Database of certified products "OK biodegradable SOIL" and "OK compost HOME", Website accessed on 08-01-2021*. Available from: https://www.tuv-at.be/green-marks/certified-products/.
54. DIN CERTCO. *Database of certified products "Biodegradable in soil", Website accessed on 08-01-2021*. Available from: https://www.dincertco.de/din-certco/en/main-navigation/certificates-and-registrations/the-din-certco-database/.
55. Rychter, P., et al., *Study of aliphatic-aromatic copolyester degradation in sandy soil and its ecotoxicological impact.* Biomacromolecules, 2010. **11**(4): p. 839-847.
56. Kijchavengkul, T., et al., *Atmospheric and soil degradation of aliphatic-aromatic polyester films.* Polymer Degradation and Stability, 2010. **95**(2): p. 99-107.
57. Weng, Y.X., et al., *Biodegradation behavior of poly(butylene adipate-co-terephthalate) (PBAT), poly(lactic acid) (PLA), and their blend under soil conditions.* Polymer Testing, 2013. **32**(5): p. 918-926.
58. de Oliveira, T.A., et al., *Biodegradation of mulch films from poly(butylene adipate co-terephthalate), carnauba wax, and sugarcane residue.* Journal of Applied Polymer Science, 2019. **136**(47).
59. Mueller, R.J., *Biological degradation of synthetic polyesters-Enzymes as potential catalysts for polyester recycling.* Process Biochemistry, 2006. **41**(10): p. 2124-2128.
60. Krueger, M.C., H. Harms, and D. Schlosser, *Prospects for microbiological solutions to environmental pollution with plastics.* Applied Microbiology and Biotechnology, 2015. **99**(21): p. 8857-8874.
61. Brown, D.W., R.E. Lowry, and L.E. Smith, *Kinetics of Hydrolytic Aging of Polyester Urethane Elastomers.* Macromolecules, 1980. **13**(2): p. 248-252.
62. Albertsson, A.-C. and O. Ljungquist, *Degradable Polymers. I. Synthesis, Characterization, and Long-Term in Vitro Degradation of a 14C-Labeled Aliphatic Polyester.* Journal of Macromolecular Science: Part A - Chemistry, 1986. **23**(3): p. 393-409.
63. Baba, H., et al., *Effects of Molecular Structure on Enzymatic Degradation of Polyesters.* Nippon Kagaku Kaishi, 1992. **1992**(5): p. 527-533.
64. Mochizuki, M., et al., *Structural effects upon enzymatic hydrolysis of poly(butylene succinate-co-ethylene succinate)s.* Macromolecules, 1997. **30**(24): p. 7403-7407.
65. Cho, K., J. Lee, and K. Kwon, *Hydrolytic degradation behavior of poly(butylene succinate)s with different crystalline morphologies.* Journal of Applied Polymer Science, 2001. **79**(6): p. 1025-1033.
66. Shirahama, H., et al., *Synthesis and enzymatic degradation of high molecular weight aliphatic polyesters.* Journal of Applied Polymer Science, 2001. **80**(3): p. 340-347.
67. Montaudo, G. and P. Rizzarelli, *Synthesis and enzymatic degradation of aliphatic copolyesters.* Polymer Degradation and Stability, 2000. **70**(2): p. 305-314.
68. Ahn, B.D., et al., *Synthesis and characterization of the biodegradable copolymers from succinic acid and adipic acid with 1,4-butanediol.* Journal of Applied Polymer Science, 2001. **82**(11): p. 2808-2826.
69. Sato, H., et al., *A novel evaluation method for biodegradability of poly(butylene succinate-co-butylene adipate) by pyrolysis-gas chromatography.* Polymer Degradation and Stability, 2001. **73**(2): p. 327-334.
70. Nikolic, M.S. and J. Djonlagic, *Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene adipate)s.* Polymer Degradation and Stability, 2001. **74**(2): p. 263-270.
71. Lindström, A., A.-C. Albertsson, and M. Hakkarainen, *Quantitative determination of degradation products an effective means to study early stages of degradation in linear and branched poly(butylene adipate) and poly(butylene succinate).* Polymer Degradation and Stability, 2004. **83**(3): p. 487-493.
72. Tserki, V., et al., *Biodegradable aliphatic polyesters. Part II. Synthesis and characterization of chain extended poly(butylene succinate-co-butylene adipate).* Polymer Degradation and Stability, 2006. **91**(2): p. 377-384.

73. Pan, W., et al., *Enzymatic degradation of poly(butylene succinate) with different molecular weights by cutinase.* International Journal of Biological Macromolecules, 2018. **111**: p. 1040-1046.

74. Tokiwa, Y. and T. Suzuki, *Hydrolysis of polyesters by lipases.* Nature, 1977. **270**(5632): p. 76-78.

75. Hayase, N., et al., *Isolation and characterization of poly(butylene succinatec-o-butylene adipate)-degrading microorganism.* Journal of Bioscience and Bioengineering, 2004. **97**(2): p. 131-133.

76. Hemashenpagam, N., et al., *Isolation and characterization of a bacterium that degrades PBSA.* International Journal of Pharma and Bio Sciences, 2013. **4**(4): p. B335-B342.

77. Hongsriphan, N. and P. Arak, *Properties of Agricultural Films Prepared from Biodegradable Poly(Butylene Succinate) Adding Natural Sorbent and Fertilizer.* Journal of Polymers and the Environment, 2019. **27**(2): p. 434-443.

78. Al Hosni, A.S., J.K. Pittman, and G.D. Robson, *Microbial degradation of four biodegradable polymers in soil and compost demonstrating polycaprolactone as an ideal compostable plastic.* Waste management (New York, N.Y.), 2019. **97**: p. 105-114.

79. Zhang, M., et al., *Biodegradability of PBS/PHB blends.* Gaofenzi Cailiao Kexue Yu Gongcheng/Polymeric Materials Science and Engineering, 2010. **26**(7): p. 43-46.

80. Zhang, S.J., Y.W. Tang, and L.H. Cheng, *Biodegradation behavior of PLA/PBS blends*, in *Advanced Materials Research*. 2013. p. 937-940.

81. Liu, L., et al., *Biodegradability of poly(butylene succinate) (PBS) composite reinforced with jute fibre.* Polymer Degradation and Stability, 2009. **94**(1): p. 90-94.

82. Kim, H.S., et al., *Biodegradability of bio-flour filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil.* Polymer Degradation and Stability, 2006. **91**(5): p. 1117-1127.

83. Narancic, T., et al., *Biodegradable Plastic Blends Create New Possibilities for End-of-Life Management of Plastics but They Are Not a Panacea for Plastic Pollution.* Environmental Science and Technology, 2018. **52**(18): p. 10441-10452.

84. TÜV Austria Belgium. *Database of certified products "OK compost INDUSTRIAL" and "Seedling", Website accessed on 08-01-2021*. Available from: https://www.tuv-at.be/green-marks/certified-products/.

85. DIN CERTCO. *Database of certified products "Industrial compostable", Website accessed on 08-01-2021*. Available from: https://www.dincertco.de/din-certco/en/main-navigation/certificates-and-registrations/the-din-certco-database/.

86. Itävaara, M., S. Karjomaa, and J.-F. Selin, *Biodegradation of polylactide in aerobic and anaerobic thermophilic conditions.* Chemosphere, 2002. **46**(6): p. 879-885.

87. Lunt, J., *Large-scale production, properties and commercial applications of polylactic acid polymers.* Polymer Degradation and Stability, 1998. **59**(1): p. 145-152.

88. Södergård, A., J.F. Selin, and J.H. Näsman, *Hydrolytic degradation of peroxide modified poly(L-lactide).* Polymer Degradation and Stability, 1996. **51**(3): p. 351-359.

89. Day, M., et al., *Degradable polymers: The role of the degradation environment.* Journal of Environmental Polymer Degradation, 1997. **5**(3): p. 137-151.

90. Siparsky, G.L., et al., *Water transport in polylactic acid (PLA), PLA/polycaprolactone copolymers, and PLA/polyethylene glycol blends.* Journal of Environmental Polymer Degradation, 1997. **5**(3): p. 125-136.

91. Karjomaa, S., et al., *Microbial degradation of poly-(L-lactic acid) oligomers.* Polymer Degradation and Stability, 1998. **59**(1-3): p. 333-336.

92. Satti, S., et al., *Biodegradation of Poly(lactic acid) in Soil Microcosms at Ambient Temperature: Evaluation of Natural Attenuation, Bio-augmentation and Bio-stimulation.* Journal of Polymers and the Environment, 2018.

93. Satti, S.M., et al., *Isolation and characterization of bacteria capable of degrading poly(lactic acid) at ambient temperature.* Polymer Degradation and Stability, 2017. **144**: p. 392-400.

94. Decorosi, F., et al., *The degradative capabilities of new Amycolatopsis isolates on polylactic acid.* Microorganisms, 2019. **7**(12).

95. Saadi, Z., et al., *Fungal Degradation of Poly(l-lactide) in Soil and in Compost.* Journal of Polymers and the Environment, 2012. **20**(2): p. 273-282.

96. Apinya, T., N. Sombatsompop, and B. Prapagdee, *Selection of a Pseudonocardia sp. RM423 that accelerates the biodegradation of poly(lactic) acid in submerged cultures and in soil microcosms.* International Biodeterioration and Biodegradation, 2015. **99**: p. 23-30.

97. Lipsa, R., et al., *Biodegradation of poly(lactic acid) and some of its based systems with Trichoderma viride.* International Journal of Biological Macromolecules, 2016. **88**: p. 515-526.

98. Molenveld, K. and H. Bos, *Biobased Plastics 2019, Groene grondstoffen No. 21, ISBN: 978-94-6343-541-3*. 2019, Propress: Wageningen. p. 70.

99. Sudesh, K., et al., *Polyhydroxyalkanoates*, in *Handbook of Biodegradable Polymers*. 2020, De Gruyter: Berlin. p. 183-216.

100. Ienczak, J.L. and G.M.F. Aragão, *Biotechnologically Produced Biodegradable Polyesters*, in *Handbook of Biodegradable Polymers*, L. A. and S. A., Editors. 2011, Whiliey. p. 23-44.
101. Tan, G.A., et al., *Start a research on biopolymer polyhydroxyalkanoate (PHA): A review.* Polymers, 2014. **6**(3): p. 706-754.
102. Schneider, A.L.S., et al., *Biodegradation of Poly(3-Hydroxybutyrate) Produced from Cupriavidus necator with Different Concentrations of Oleic Acid as Nutritional Supplement.* Journal of Polymers and the Environment, 2010. **18**(3): p. 401-406.
103. Mergaert, J., et al., *Biodegradation of polyhydroxyalkanoates.* FEMS Microbiology Letters, 1992. **103**(2-4): p. 317-321.
104. Jendrossek, D., *Microbial degradation of polyesters: A review on extracellular poly(hydroxy alkanoic acid) depolymerases.* Polymer Degradation and Stability, 1998. **59**(1-3): p. 317-325.
105. Jendrossek, D., A. Schirmer, and H.G. Schlegel, *Biodegradation of polyhydroxyalkanoic acids.* Applied Microbiology and Biotechnology, 1996. **46**(5-6): p. 451-463.
106. Khanna, S. and A.K. Srivastava, *Computer simulated fed-batch cultivation for over production of PHB: A comparison of simultaneous and alternate feeding of carbon and nitrogen.* Biochemical Engineering Journal, 2006. **27**(3): p. 197-203.
107. La Mantia, F.P., et al., *Degradation of polymer blends: A brief review.* Polymer Degradation and Stability, 2017. **145**: p. 79-92.
108. Tsuji, H., A. Mizuno, and Y. Ikada, *Blends of aliphatic polyesters. III. Biodegradation of solution-cast blends from poly(L-lactide) and poly(ε-caprolactone).* Journal of Applied Polymer Science, 1998. **70**(11): p. 2259-2268.
109. Dharmalingam, S., et al., *Soil Degradation of Polylactic Acid/Polyhydroxyalkanoate-Based Nonwoven Mulches.* Journal of Polymers and the Environment, 2015. **23**(3): p. 302-315.
110. Navarro-Baena, I., et al., *Design of biodegradable blends based on PLA and PCL: From morphological, thermal and mechanical studies to shape memory behavior.* Polymer Degradation and Stability, 2016. **132**: p. 97-108.
111. Lv, S., et al., *Microstructure analysis of polylactic acid-based composites during degradation in soil.* International Biodeterioration and Biodegradation, 2017. **122**: p. 53-60.
112. Awale, R.J., et al., *Enhanced flexibility of biodegradable polylactic acid/starch blends using epoxidized palm oil as plasticizer.* Polymers, 2018. **10**(9).
113. Palsikowski, P.A., et al., *Biodegradation in Soil of PLA/PBAT Blends Compatibilized with Chain Extender.* Journal of Polymers and the Environment, 2018. **26**(1): p. 330-341.
114. Liu, Y., et al., *Accelerated biodegradation of PLA/PHB-blended nonwovens by a microbial community.* RSC Advances, 2019. **9**(18): p. 10386-10394.
115. Hayes, D.G., et al., *Effect of diverse weathering conditions on the physicochemical properties of biodegradable plastic mulches.* Polymer Testing, 2017. **62**: p. 454-467.
116. Kijchavengkul, T., et al., *Assessment of aliphatic-aromatic copolyester biodegradable mulch films. Part I: Field study.* Chemosphere, 2008. **71**(5): p. 942-953.
117. Kijchavengkul, T., et al., *Assessment of aliphatic-aromatic copolyester biodegradable mulch films. Part II: Laboratory simulated conditions.* Chemosphere, 2008. **71**(9): p. 1607-1616.
118. Hablot, E., et al., *Effect of Simulated Weathering on Physicochemical Properties and Inherent Biodegradation of PLA/PHA Nonwoven Mulches.* Journal of Polymers and the Environment, 2014. **22**(4): p. 417-429.

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Report 2138
ISBN 978-94-6395-760-1

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