

## Final Report

# WP4 – Comparison between natural and synthetic polymers

Cefic-LRI ECO52 project

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## Acronyms and Abbreviations

DegT50	Degradation time 50
DT50	Disappearance time 50
ISO	International Organization for Standardization
MP	Microplastics
NP	Nanoplastics
OECD	Organization for Economic Co-operation and Development
P	persistent
PAM	Cationic polyacrylamide copolymers
PBS	Polybutylensuccinat
PBSA	Poly(butylene succinate-co-butylene adipate)
PBT	persistent, bioaccumulative, toxic
PCL	Polycaprolactone
PE	Polyethylene
PEG	Polyethyleneglycols
PET	Poly(ethylene terephthalate)
PHB	Poly(3-hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA or PLLA	Poly(lactic acid)
PQ	Polyquaternium
PP	Polypropylene
PS	Polystyrene
PVC	Poly(vinyl chloride)
PVA	Poly(vinyl alcohol)
PVP	Poly(vinyl pyrrolidone)
RAC	Risk Assessment Committee
UVCB	Substances of unknown or variable composition, complex reaction products or biological materials
vP	very persistent
vPvB	very persistent, very bioaccumulative

# 1 Introduction and objectives

Polymers<sup>1</sup> are “a class of natural or synthetic substances composed of very large molecules, called macromolecules, that are multiples of simpler chemical units called monomers”. According to IUPAC<sup>2</sup> polymers are: “Substances composed of macromolecules, very large molecules with molecular weights ranging from a few thousand to as high as millions of grams/mole.” And OECD<sup>3</sup> defines a polymer as: “A 'POLYMER' means a substance consisting of molecules characterized by the sequence of one or more types of monomer units and comprising a simple weight majority of molecules containing at least three monomer units which are covalently bound to at least one other monomer unit or other reactant and consists of less than a simple weight majority of molecules of the same molecular weight. Such molecules must be distributed over a range of molecular weights wherein differences in the molecular weight are primarily attributable to differences in the number of monomer units. In the context of this definition a 'MONOMER UNIT' means the reacted form of a monomer in a polymer.”

A similar definition as published by OECD is also used under REACH. In accordance with REACH (Article 3(5)), a polymer is defined as a substance meeting the following criteria (ECHA, 2012): “...

- (a) Over 50 percent of the weight for that substance consists of polymer molecules; and,
- (b) The amount of polymer molecules presenting the same molecular weight must be less than 50 weight percent of the substance.

*In the context of this definition: a "polymer molecule" is a molecule that contains a sequence of at least 3 monomer units, which are covalently bound to at least one other monomer unit or other reactant. ...”*

In addition, polymers make up many of the materials in living organisms. These so-called natural polymers are for example, cellulose, chitin, protein, carbohydrates such as starches etc. Natural polymers are regarded as no concern for the environment. Natural polymers are integral parts of the environment and though they might not meet current regulatory requirements, e.g. with regard to degradability, it is proven that they don't accumulate there over time.

In this report it will be evaluated how natural polymers behave under standard laboratory degradation conditions and providing potential benchmarks for man-made polymers. Further, the similarities and differences between natural and synthetic polymers are in the focus. The available information on degradation of some natural and synthetic polymers under different conditions are compared, whereby literature data are preferred using standardized testing methods, and which compares the degradation potential of different polymer sources using the same method.

The following questions are considered:

- Which are the mechanisms to break down natural or synthetic polymers under environmental conditions?
- Can results from standard ready biodegradability tests or simulation tests for these substance groups be extrapolated to real environmental conditions, and is this different for natural vs synthetic polymers? Which adaptations are necessary?
- Is the bioavailability (or surface area) as most important factor influencing test results on degradation different for natural vs synthetic polymers?
- How this matches with the protection goal and criteria for the persistence framework.

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<sup>1</sup> <https://www.britannica.com/science/polymer>

<sup>2</sup> <https://iupac.org/polymer-edu/what-are-polymers>

<sup>3</sup> <http://www.oecd.org/env/ehs/oecddefinitionofpolymer.htm>

This document is part of a series of reports produced as part of the Cefic-LRI ECO52 project: 'Expanding the conceptual principles and applicability domain of persistence screening and prioritization frameworks, including single constituents, polymers, and UVCBs.'

## 2 Types of polymers

Generally, polymeric substances and materials can be grouped on their chemistry or structure. **Structural descriptors** are for example chemical formula, degree of substitution, tacticity, weight-average molecular weight (Mw), polydispersity, number-average molecular weight (Mn), and reactive functional groups (ECETOC, 2020). Main types of polymers are Polyolefine, Polyester, Polyether, Polyurethane, etc.. However, even one class of substance such as Polyethylene (PE) could be divided in several sub-groups such as low density PE (LDPE) or high-density PE (HDPE) with significant different properties (Andrady, 2017).

Another option to categorize the polymers is based on **morphological descriptors** (e.g. physical state, shape, degree of crystallinity, particle size, etc) or on **physico-chemical properties** (e.g. water solubility, viscosity / melt-flow index / glass transition temperature, density, etc.).

Overall, the nature of a polymer product having multiple components drives the determination of all structural and morphological descriptors and physico-chemical properties of polymers (ECETOC, 2020).

Finally, polymers can roughly be divided into **fossil-based** and **bio-based** polymers, i.e. polymers for which bioresources have been used for manufacturing. Bioplastics are either bio-based or biodegradable, or both (European Bioplastics, 2018), which can be illustrated in a material coordinate system of plastics as given in Figure 1. An additional group are **natural polymers or biopolymers**, i.e. polymers which are made in nature. These natural polymers are expected to be biodegradable under environmental conditions, and thus are mostly part of the group of biodegradable bioplastics.

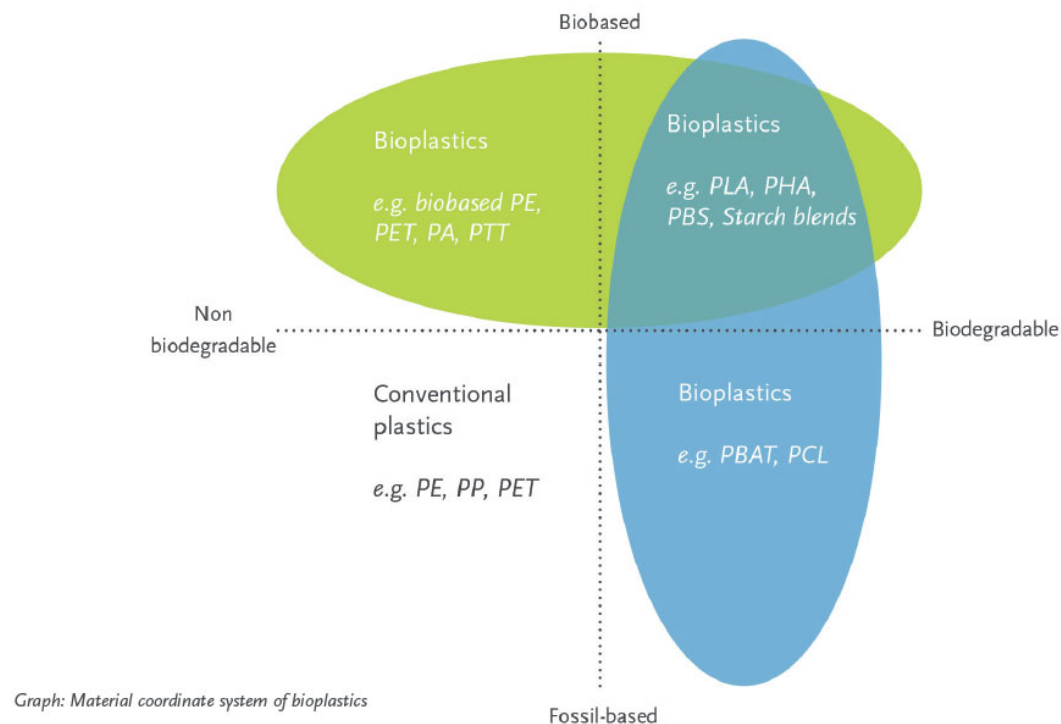


Figure 1: Material coordinate system of plastics according to European Bioplastics (2018)

## 2.1 Natural polymers

Polymers exist in nature as well. These so-called natural polymers (or biopolymers) include natural rubber, cellulose, hemicellulose, starch, lignin, chitin, cutin. Sometimes they will be used as food additive such as glucomannan, agar, pectin, inulin, rosin, guar gum, locust bean gum, gum acacia, karaya gum, gum tragacanth, alginates, carageenans, psyllium and xanthum gum.

Some examples for natural polymers and their source and structural and/or morphological descriptors are given in the following (not exhaustive):

**Starch** (Kögel-Knabner, 2002; Polman et al., 2020):

- produced by most green plants for energy storage, and (major) ingredient in wheat, potatoes, maize (corn), and rice.
- polysaccharide; branched amylopectin and linear amylose chains; weak  $\alpha$ -glycosidic bonds
- granular shape, alternating amorphous and semi crystalline layers
- white, tasteless and odorless powder; insoluble in cold water or alcohol

**Cellulose** (Klemm et al., 2005; Polman et al., 2020):

- plant cell walls
- polysaccharide ( $C_6H_{10}O_5$ )<sub>n</sub>; stronger  $\beta$ -glycosidic linkages; linear chain with degree of polymerization (DP) values of several hundred to many thousand depending on the origin and treatment
- crystalline (but small fraction amorphous)
- tasteless and odourless; hydrophilic; insoluble in water and most organic solvents

**Lignin** (Datta et al., 2017; Polman et al., 2020):

- plant cell walls, especially in wood and bark
- consists of the aromatic coniferyl, coumaryl and sinapyl alcohols, bound together by C-O-C or C-C linkages; about 50% of these are the  $\beta$ -O-4 aryl ether type
- amorphous three-dimensional polymer
- insoluble

**Cutin** (Briggs, 1999; Riederer and Schonherr, 1988):

- component of the plant cuticle
- composed of various characteristic long-chain (C16 and C18) alkanolic acids (most of them saturated) substituted by hydroxy, carbonyl, and epoxy groups; polyester polymer consisting of omega hydroxy acids and their derivatives
- lipid, waxy polymer
- insoluble in organic solvents; water resistant (hydrophob, lipophilic)

**Natural rubber**

- elastomer made from latex, a sticky, milky tree sap
- cis-1,4-polyisoprene; allylic C-H bonds in each repeat unit
- strain crystallization
- not easily soluble

Overall, natural polymers could have different structural linkages and a high variety of molecular weights. Often they are polysaccharides or its derivatives with weak  $\alpha$ -glycosidic bonds or stronger  $\beta$ -glycosidic linkages. The biopolymers could exist crystalline, semi-crystalline or amorphous, are often insoluble, and can be hydrophilic but also hydrophobic. Thus different structural and morphological descriptors and physico-chemical properties can be assigned. Based on these descriptors and



properties, some polymers are expected to be hydrolytically more stable than others, and it is obvious that they will have different potential for (bio)degradation.

## 2.2 Modified biopolymers

Natural polymers are often modified to get higher stability for (industrial) uses. These type of bioplastics are produced from a range of natural resources, such as corn, cassava, cotton linters, or flax fibres, and agricultural by-products such as rice straw (Polman et al., 2020). The structure resemble the biopolymers they are based on.

Commonly used modified biopolymers are for example thermoplastic starch (TPS), cellulose acetate (CA) and lignin-based polymers (Polman et al., 2020).

### **Thermoplastic starch and starch blends:**

Starch is renewable, cheap, and abundantly available biopolymer. However, the intermolecular forces and hydrogen bonds in starch resist it to be processed as a thermoplastic material (Khan et al., 2017). To overcome this issue, starch will be modified to get a material called thermoplastic starches (TPSs). During the TPS production process starch loses its natural granular shape and crystalline structure (Polman et al., 2020). This process of destructure is achieved by exposing starch grains to heat and shear in combination with the addition of a plasticizer. The plasticizer breaks and replaces the hydrogen bonds between the starch polymers, which enables the polymer chains to move more freely (Nafchi et al., 2013; Polman et al., 2020).

Starch blends are often mentioned in the literature as well. These are usually blends of TPS with traditional polymers. These were prepared in efforts to obtain new materials with low cost and high biodegradability (Kaseem et al., 2012). Please note, these are also blends with non-biodegradable polymers such as PE, PP or PS, but also biodegradable polymers such as polylactic acid (PLA) will be used.

### **Cellulose acetate**

Cellulose acetate (CA) is an organic polyester produced by the acetylation of cellulose fibres from different plant residues such as rye, rice straw, cotton, wheat or wood fibre (Polman et al., 2020). During the acetylation, a hydrogen atom in the cellulose is replaced with an acetyl group. The extent to which substitution takes place is called the degree of substitution (DS), which is the amount of acetyl groups per monomer (Haske-Cornelius et al., 2017). The DS has a significant influence on the properties of CA, and probably also on the potential for biodegradation.

### **Lignin-based polymers:**

Lignin is subject to condensation reactions under high temperatures, which gives the material thermosetting properties (Polman et al., 2020). At the moment, a first generation of lignin-based thermoplastics is commercially available (Wang et al., 2016), which consists of lignin, cellulose and natural additives. In addition, lignin containing fibres are used in other bioplastics such as TPS.

## 2.3 Synthetic polymers

Synthetic polymers are intentionally produced as such in factory to take advantage of their properties during use. They could be fossil-based or bio-based. If the identical synthetic polymer is manufactured from either natural sources or from petroleum, the same biodegradability is expected due to the same chemical properties.

The synthetic polymers cover a wide range of structural possibilities. These could be carbohydrates polymers such as polyolefines (PE, PP), or polystyrol (PS), but also with heteroatoms, such as polyvinylchloride (PVC), polyesters such as polyethyleneterephthalate (PET), polyether, polyamide such as Nylon 6, etc.

Plastic materials have a wide range of densities (0.01 to 2.3 g/cm<sup>3</sup>; (Duis and Coors, 2016), although it is worth noting that densities of plastic items can be modified by additives and environmental processes such as weathering and fouling. Although the majority of polymers (e.g. plastics) are immiscible in water, there are some water soluble polymers such as Polyethyleneglycols [PEG], Poly(vinyl alcohol) [PVA] or Poly(vinyl pyrrolidone) [PVP], anionic homo- and copolymers of acrylic acid, and cationic polyquaterniums [PQs] (Bernhard et al., 2008; Duis et al., 2021; Eubeler, 2010).

Finally, there are also synthetic polymers on the market which are assumed to be biodegradable such as the polyesters polyhydroxyalkanoates (PHAs), of which polyhydroxybutyrate (PHB) is most commonly used, polylactic acid (PLA), polycaprolactone (PCL), or polybutylene succinate (PBS). PHA are also biopolymers, but made in factory as well.

## 2.4 Summary

Several types of polymers are on the market, and different possibilities exist to categorize these polymers. Besides the grouping based on structural, morphological properties, or physico-chemical properties, the polymers could be grouped based on the source: natural polymers (or biopolymers), modified biopolymers, or synthetic polymers. Another option is to (sub)group the synthetic polymers into bio-based or fossil-based polymers. Finally, the polymers could be grouped into biodegradable or not biodegradable.

Bio-plastic (Bio-based and/or biodegradable plastics)					
Biopolymers Natural polymers (made in nature)	Bio-based polymers (made in factory)			petroleum-based polymers (made in factory)	
	Modified biopolymers	Bio-based	Blends	fossil-based, biodeg	conventional
Starch	thermoplastic starch	PLA (Polylactic acid)	starch blends (e.g. Mater-Bi)	PBS(A)	PE
Cellulose	cellulose acetate	bio-PBS(A) (Polybutylene succinate (adipate))	ecovio	PVA	PP
Lignin	lignin based bioplastic	Bio-PCL (Poly(ε-caprolactone))	Starch/PE blends	PBAT	PET
Chitin		PHA (Polyhydroxyalkanoates)	...	PCL	...
Pektin		bio-PE, bio-PP, bio-PA	Water soluble	...	
Apple wax/Cutin		bio-PET, bio-PTT, PEF	PEG		
Natural rubber		...	PAM		
Polyhydroxyalkanoates					

Figure 2: Grouping of polymers (assumed to be biodegradable (green), not biodegradable (red), partly biodegradable (orange))

### 3 Specific standardized methods for testing degradability of plastics and polymers

Recommended OECD guidelines for measurement of biodegradability were developed to assess small, soluble molecules, and not developed to measure the biodegradation of polymers. Polymers are usually not used in interlaboratory validation studies for those guidelines nor are polymers recommended as reference substances. Further validation needs to be undertaken and appropriate reference substances (e.g. natural polymers such as cellulose as performance benchmarks) are required if such tests should get any value in assessing the persistence of polymers. It is recognized that sometimes information on conditions how to apply solid materials is given, for example in OECD 301 Annex III (OECD, 1992) *“it is recommended that solid materials be homogenised by appropriate means to avoid errors due to non-homogeneity”*. However, for polymers more detailed recommendations on preparation methods and assessment of influence of particle size after homogenisation is required.

In recent years several specific standard protocols have been adapted or developed for (bio)degradability testing of plastic materials. These specific standards have already been reviewed in several reports and articles (Briassoulis and Dejean, 2010; ECETOC, 2020; ECHA, 2020; Eubeler, 2010; Eubeler et al., 2009; Kjeldsen et al., 2019; Ruggero et al., 2019). The available standards are mainly ISO or ASTM guidelines, which are often to a large extent identical and very similar.

With focus on ISO guidelines the relevant guidelines are:

- Specific guidance for **test sample preparation** is given in ISO 10210 (ISO, 2012).
- Guidance to calculate the mineralization rate considering **specific surface area** is given in ISO 5148 (ISO, 2021a).
- ISO/TS 19022 (ISO, 2016b) presents a method of controlled acceleration of laboratory **weathering** by increased irradiance. Changes in colour can be determined using ISO 4582 (ISO, 2017); tensile properties can be determined using ISO 527 (ISO, 2019a). Chemical changes are analysed primarily by IR spectroscopy, with additional analyses using UV/visible spectroscopy during the photoageing of polymers (ISO 10640; ISO (2011)).
- Biodegradability of plastic materials in an **aqueous medium** is given in ISO 14851 and ISO 14852 (ISO, 2018, 2019b).
- Biodegradability of plastic materials in **soil** is given in ISO 17566 (ISO, 2019c). Additionally ISO 23517 (ISO, 2021b) or DIN EN 17033 (DIN, 2018) specify test methods and evaluation criteria for the ultimate aerobic biodegradation of mulch films.
- ISO 22403 (ISO, 2020b) specifies test methods and evaluation criteria for the **marine environment**. Biodegradability of plastic materials in seawater is given in ISO 23977 (ISO, 2020d, e) or seawater/sediment interface in ISO 18830 and 19679 (ISO, 2016a, 2020a) or sediment in ISO 22404 (ISO, 2019d). Additionally, ISO 23832 (ISO, 2021c) determines the degradation rate and the disintegration degree, and ISO 22766 (ISO, 2020c) gives information for testing under real field conditions.
- **Combination** of weathering and (bio)degradation has been described for example in ASTM D7991-15. Framework is given in ASTM D6954-18 (ASTM, 2018a).

In addition, several guidelines are available to determine the biodegradation of plastic materials under anaerobic conditions, in sewage treatment plants, or during composting.

### 3.1 Weathering

When a polymeric material is exposed under natural outdoor weathering or artificial weathering conditions, UV radiation and other moderate environmental stresses can result in a chemical ageing, and a change in physical properties.

Several standard test systems (ISO and ASTM) have been developed to consider and evaluate the effects of weathering. For example ISO/TS 19022 presents a method of controlled acceleration of laboratory weathering by increased irradiance.

In ISO/TS 19022 (ISO, 2016b), *“the base level test shall use weathering parameters (irradiance, temperatures, relative humidity) which are not above a maximum natural level (e.g. irradiance in the wavelength range 300 nm to 400 nm smaller than 66 W/m<sup>2</sup>). As a second step, the irradiance is increased step by step above the natural level.”* In this test the test results (property changes) should be plotted as a function of the radiant exposure.

The changes during photoageing can be followed by determining

- changes in colour (ISO 4582; ISO (2017))
- other methods for appearance, mechanical or other properties; for example tensile properties can be determined using ISO 527 (ISO, 2019a).
- chemical changes by weathering are analysed primarily by IR spectroscopy, with additional analyses using UV/visible spectroscopy during the photoageing of polymers (ISO 10640; ISO (2011)).

### 3.2 Freshwater

Biodegradability of plastic materials in an aqueous medium can be determined according to ISO 14851 and ISO 14852. The first one is using oxygen consumption and the second one carbon dioxide evolution, but the guidelines are in principle equivalent.

ISO 14851 (BOD) or 14852 (CO<sub>2</sub>):

- 20–25 °C (±1 °C),
- inoculum from WWTP, use suspended solids in the range of 30 mg/l to 1000 mg/L in the final mixture
- duration: maximum 2 month
- test material: 100 mg/l TOC; preferably powder (< 250 µm) but also films, pieces, fragments and shaped articles
- reference material: aniline and/or well-defined biodegradable polymer (microcrystalline cellulose, ashless cellulose filters, or poly-β-hydroxybutyrate): validity criteria > 60% at end, negative control: non-biodegradable polymer (e.g. PE)
- result: degree of mineralization

### 3.3 Soil

Guideline for measurement of biodegradability of plastic materials in soil is available with ISO 17566 (ISO, 2019c) and ASTM 5998 (ASTM, 2018b). Both guidelines are similar; in the ASTM it is mentioned that it is equivalent to ISO 17556. Biodegradation is determined by measuring oxygen demand in a respirometer or the amount of carbon dioxide evolved.

ISO 17556 (BOD or CO<sub>2</sub>):

- 20-28 °C (±2 °C)
- mature compost added to increase biomass (40 g/kg)
- duration: typically 6 month (up to 2 years);
- test material: 200 mg test material on 200 g soil, preferably powder (< 250 µm) but also films (5x5 mm), fragments and shaped articles
- reference material: well-defined biodegradable polymer {microcrystalline-cellulose powder, ashless cellulose filters or poly-(R)-3-hydroxybutyrate [(R)-PHB]}; validity criteria: > 60% at plateau (ISO), > 70% in 120 days (ASTM), negative control non-biodegradable polymer (e.g. PE)
- result: degree of mineralization

Additionally ISO 23517 (ISO, 2021b) or DIN EN 17033 (DIN, 2018) specify test methods and evaluation criteria for the ultimate aerobic biodegradation of mulch films. It should be noted that mulch films are (finished) articles not a substance.

ISO 23517 or ISO 17033 (biodegradable mulch films):

- reference to ISO 17556
- without pre-treatment by heat and or an exposure to radiation exposure
- result: > 90% absolute or relative to reference material

ISO 23517 and ISO 17033 are not describing the test method in detail. They give reference to ISO 17566, and added only information on the evaluation criteria and requirements regarding constituents. They address additionally the benchmarking to reference material such as cellulose. If possible, the physical form and size of the reference material should be comparable to that of the test material. Both the reference material and the test item shall be tested for the same length of time and the results compared at the same point in time.

### 3.4 Marine environment

Test methods and evaluation criteria for the assessment of the intrinsic biodegradability of plastic materials exposed to marine inocula under mesophilic aerobic laboratory conditions is specified in ISO 22403 (ISO, 2020b). The plastic material, polymer or each organic constituent separately shall be tested together with reference material and negative control according to one of the following marine biodegradation test methods: ISO 18830, ISO 19679, ISO 22404, ASTM D6691-17, ISO 23977-1, ISO 23977-2. Biodegradability is proven if mineralisation absolute or relative to reference material is at least 90 %.

In ISO 23977 (ISO, 2020d, e) the methods are described for **seawater**. Part 1 determines the aerobic biodegradability by analysing the evolved carbon dioxide, whereas Part 2 measures the oxygen demand.

ISO 23977 (BOD or CO<sub>2</sub>):

- preferably between 15 °C to 25 °C, but not exceeding 28 °C, to an accuracy of  $\pm 1$  °C, in the dark or diffused light
- inoculum: 90 ml of natural seawater (“pelagic seawater test”) or 90 ml of natural seawater to which sediment of 0,1 g/l to 1,0 g/l (wet weight) has added (“suspended sediment seawater test”)
- test material: at least 100 mg/L (60 mg/L TOC); powder (< 250  $\mu$ m) or film. Similar particle sizes of powder should preferably be used in the test; similar shapes and thicknesses of the films should preferably be used if different kinds of plastic materials are to be compared.
- reference material: microcrystalline cellulose or ashless cellulose filters, TOC, form, and size should be comparable to that of the test material, validity criteria > 60% after 180 days; negative control: non-biodegradable polymer (e.g. PE), same form as test material, validity criteria < 10% after 180 days
- duration: typically not exceed 1 year ( test may be extended, but not to longer than 2 years)
- result: degree of mineralization (mean value at plateau or highest value)

ISO 18830 and 19679 (ISO, 2016a, 2020a) contain the methods for the measurement of the biodegradation of non-floating plastic material in **seawater/sediment** interface. Again, one for carbon dioxide evolved and one for oxygen demand. A standard for **sediment** is given with ISO 22404 (ISO, 2019d), and this method uses the analysis of the carbon dioxide evolved.

ISO 18830 (BOD), ISO 19679 (CO<sub>2</sub>):

- preferably between 15 °C to 25 °C, but not exceeding 28 °C, to an accuracy of  $\pm 2$  °C, in the dark or diffused light
- inoculum: natural seawater and sediment with a water/sediment volume ratio between 3:1 and 5:1 and a sediment layer of about 0.3 cm to 0.5 cm depending on the granulometry
- test material: at least 100 mg/L (ThOD 170 mg/L or TOC 60 mg/L), 150 – 300 mg/L recommended; film or sheet, similar shapes and thicknesses should preferably be used if different kinds of plastic materials are to be compared. (powder may be used but critical as difficult to keep the powder settled)
- reference material: ashless cellulose filters, TOC, form, and size should be comparable to that of the test material, validity criteria > 60% after 180 days; optionally negative control: non-biodegradable polymer (e.g. PE), same form as test material, validity criteria no significant amount of BOD or < 10% after 180 days
- duration: typically not exceed 1 year (test may be extended, but not to longer than 2 years)
- result: degree of mineralization (mean value at plateau or highest value)

ISO 22404 (CO<sub>2</sub>):

- preferably between 15 °C to 25 °C, but not exceeding 28 °C, to an accuracy of  $\pm 2$  °C, in the dark
- inoculum: natural seawater/sediment and eliminate excess seawater before test
- test material: at least 25 mg/100g (TOC 15 mg/kg), 40-75 mg/100 g recommended; preferably powder (< 250  $\mu$ m) or as film or sheet, similar shapes and thicknesses should preferably be used if different kinds of plastic materials are to be compared.
- reference material: microcrystalline cellulose or ashless cellulose filters, TOC, form, and size should be comparable to that of the test material, validity criteria > 60% after 180 days; optionally negative control: non-biodegradable polymer (e.g. PE), same form as test material, validity criteria no significant amount (< 10%) after 180 days
- duration: maximum 2 years
- result: degree of mineralization (mean value at plateau or highest value)

Additionally, ISO 23832 (ISO, 2021c) gives information about the test methods for determination of the degradation rate and the disintegration degree.

Degradation rates are determined by linear regression of the plot of the measurements (mass, thickness or tensile strength at break) referred to the respective sampling time for each sample. The regression shall be determined considering a period of at least 6 months with a minimum of 3 measured data points. All or one endpoint is used: erosion rate as decrease of thickness ( $\mu\text{m}/\text{d}$ ), or the mass loss rate as decrease of mass per unit time ( $\mu\text{g}/\text{day}$ ) or the decrease of mass per unit time per unit surface area ( $\mu\text{g}/\text{day}/\text{cm}^2$ ), or the loss of tensile properties rate as the decrease of strength at break per unit time ( $\text{Pa}/\text{day}$ ).

Assessment of disintegration is carried out with samples protected within a pocket made with a <2 mm mesh non-degradable net. The net prevents the loss of particles with dimensions higher than 2 mm. Sampling at regular intervals over testing period of 2 years; at least three replicates. Degree of disintegration is calculated based on the percent of surface area loss and mass loss.

Finally, ISO 22766 (ISO, 2020c) gives information for testing under real field conditions.

### 3.5 Combination of weathering and biodegradation

In a limited number of standards weathering and (bio)degradation has been combined. But usually, the standards recommend to measure biodegradation, physical degradation and/or mass loss in absence of sunlight.

Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation is given in ASTM D6954-18 (ASTM, 2018a). This guide presents a framework in which established ASTM standards are used in three tiers for accelerating and measuring the loss in properties and molecular weight by thermal and photooxidation processes.

In addition, ASTM D7991-15, which is the Standard Test Method for Determining Aerobic Biodegradation of Plastics Buried in Sandy Marine Sediment under Controlled Laboratory Conditions, requires plastics in a combination of water and sediment, with the option of light imitating day light and a temperature of  $15\text{--}25 \pm 2 \text{ }^\circ\text{C}$  (Meereboer et al., 2020).

### 3.6 Summary

Several standards have been developed to consider the specific needs of plastic and polymeric material. These are mainly ISO or ASTM guidelines, which are often to a large extent identical and very similar. Thereby guidelines for measurement of the biodegradation of plastic material include different compartments, e.g. aqueous medium/surface water, marine water and sediment, and soil.

The ISO (and ASTM) test guidelines are usually following the degradation via indirect sum parameters such as  $\text{O}_2$  consumption or  $\text{CO}_2$  evolution, i.e. mineralization. Relative high concentration of substance is used, and incubation at temperatures between 15 and 28  $^\circ\text{C}$ . Testing reference material is prescribed as validation criteria, e.g. cellulose is recommended in same shape and size comparable to that of the test material. As result, these standards provide the degree of mineralization at the plateaus or after a specific time; in addition, ISO 23517 and ISO 22403 give a benchmarking to reference material.

The main message can be summarized as follows:

- ✓ Metrics used in weathering (accelerated aging): usually based on changes in colour or functionality such as tensile test. Chemical changes are measured via IR or UV/VIS

- ✓ Standard methods on biodegradation of plastic materials usually based on mineralization (respirometry)
- ✓ Some standards available with further metrics on degradation rate (erosion rate, mass loss rate (mass or surface area), loss of tensile properties)
- ✓ Limited standards available for combination of weathering with biodegradation or for real field conditions



## 4 Fate of polymers in the environment

Natural polymers are part of the environment, whereas synthetic polymers are intentionally produced by mankind as such to take advantage of their properties during use and they can reach the environment (intentionally or unintentionally) after this use. In this chapter the fate of the polymers in the environment under different conditions are in the focus, especially the similarities and differences between natural and synthetic polymers. In the following available information on the presence, the distribution and degradation pathway, as well as (bio)degradation data using standardized methods or non-guideline methods will be presented and discussed.

The biodegradation of unmodified, naturally occurring biopolymers in soils has long been a research interest. The biodegradation of modified biopolymers in soils has also been investigated, but not as extensively as the degradation of unmodified biopolymers (Polman et al., 2020). For synthetic polymers, research was historically on the stability during use, but in recent years also many studies have been done on the (bio)degradation in different environmental compartments.

### 4.1 Polymers in the environment

As mentioned above and in the chapter types of polymers, natural polymers are part of the environment, e.g. starch is produced for energy storage, chitin is part of the insect exoskeleton, and cellulose, lignin, cutin are part of cell walls or plant cuticles, etc. For this reason, in the environment these biopolymers and/or their transformation products will be found in the top layer of soil. The absolute amount is a result of the equilibrium between emission to the soil and the degradation processes.

In recent years, synthetic polymers have been found in the environment in varying concentrations by several monitoring studies. For example, in a study on German rivers microplastic particle numbers varies from 2.9-214 per m<sup>3</sup>, but in other studies values up to > 10<sup>4</sup> per m<sup>3</sup> are possible (Burns and Boxall, 2018; Triebkorn et al., 2019). Microplastic was found in surface waters of urban rivers upstream and downstream of WWTP in mean particle number concentrations of 2.355 (±0.375) per m<sup>3</sup> and 5.733 (±0.850) per m<sup>3</sup>, respectively (McCormick et al., 2016). However, these numbers have to be considered with care because a recent interlaboratory study with more than 100 laboratories organised by JRC (Belz et al., 2021) proved that there is very high variability by quantification of microplastic from aqueous samples. Results obtained in the study on a reference sample don't even show a common trend, which questions the general reliability of current microplastic quantification.

Microplastic concentrations in sediment were 600,000-fold higher than in water (Scherer et al., 2020). In the marine environment floating MP counts as high as 10<sup>3</sup>-10<sup>4</sup> per m<sup>3</sup> are not uncommon in coastal regions (Andrady, 2017). Topsoils near roads and industrial areas around Sydney (Australia) might contain up to ~7% of microplastics by weight (Chae and An, 2018; Fuller and Gautam, 2016; Machado et al., 2018). No nanoplastics have been detected in natural environments to date (Jakubowicz et al., 2021). In contrast Ali et al. (2021) concluded that some studies are available which reported the occurrence of nanoplastics.

Generally, the nature of polymers being multi-constituent substances, or even UVCBs, makes quantification extremely challenging. Relatively few examples exist of the quantification of specific polymers in environmental media, either in the laboratory or the field (ECETOC, 2020).

## 4.2 Distribution and Degradation pathway of particulate polymer substances

In the environment polymeric materials are often confronted to mechanical forces and/or weathering (UV, heat, water). Weathering of plastics eventually leads to fragmentation and the creation of secondary microplastic (Andrady, 2017). Environmental weathering promotes formation of C-O bonds, which promote fragmentation or further degradation. Consequences of weathering is a yellowing discoloration, accumulation of oxidized moieties, and changes in crystallinity, which results finally in a change of mechanical properties (Andrady, 2017).

These solid polymeric substances will behave and distribute differently to (single) soluble substances. If the density is lower than or near that of water it will float on the surface or marine water. However, the plastic particles (debris) becomes encrusted with foulants, increasing in density as fouling progresses. Once the density exceeds that of (sea) water it can sink well below the water surface (Andrady, 2011). In addition, atmospheric transport plays also a role in the distribution of microplastic particles (Allen et al., 2020; Allen et al., 2019; Lehmann et al., 2021; Trainic et al., 2020).

Degradation of a particle is usually understood to be the shrinking of the mass of a particle, and complete degradation of the particle occurs if the particle completely disappears. Thereby, the compounds are sometimes not completely mineralized but transformation products will be released into the matrix. Moreover, for macromolecules built by recurring building blocks, we can expect probably a sequential degradation of chain length resulting in similar transformation products (e.g. oligomere, monomere, etc.). On the other hand, we can expect also a disintegration or fragmentation of particles. In addition, change of the surface properties could be assigned to degradation of particles as well.

According to RAC (ECHA, 2020), *“mechanical degradation or fragmentation leads to decreased particle size and increased surface area but cannot be counted as biodegradation. As a result of mechanical degradation plastic particles still remain and may accumulate in the environment.”* If it can be shown that disintegration will result in biodegradable non-persistent particles, fragmentation can be considered as a first step of plastic removal and accumulation may not be expected.

One key point is that the starting point of polymer fragmentation and degradation is often photolysis and/or hydrolysis.

**Photolysis** (UV radiation) is the most important process of weathering (Andrady, 2017). In this process the polymer or the additives such as the stabiliser can be oxidised especially in the early phases of weathering. Oxidative degradation in weathering also occurs primarily in the amorphous fraction of the plastic, and thus fragmentation tends to be in the amorphous fraction (Andrady, 2017). Weathering result also in cross-linking or chain scission, which will result in a decrease and increase of partial crystallinity, respectively (Andrady, 2017). Clearly, most conducive to rapid weathering degradation is exposure in the beach zone; compared to exposures on beach the weathering of floating plastics is considerably slower (Andrady, 2011, 2017). Even an extensively weathered, embrittled plastic material is no guarantee of subsequent biodegradability of the meso- or microplastic fragments (Andrady, 2011).

**Hydrolysis** as initial degradation step for biodegradable polymers can be divided in chemical and enzymatic hydrolysis (Brueckner et al., 2008; Su et al., 2019). Enzymes preferentially attack the amorphous parts (Brueckner et al., 2008), and amorphous or less-ordered regions degrade more easily than crystalline regions (Su et al., 2019). For Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) the introduction of 3-hydroxyvalerate has a greater amorphous region, resulting in an increased degradation rate (Meereboer et al., 2020). Enhancing the wettability by blending the matrix, may accelerate the hydrolytic degradation process. In conclusion, crystallinity and wettability will influence the biodegradation potential.

In general, the process of polymer **(bio)degradation** can be divided into four steps: i) biodeterioration, ii) depolymerisation, iii) bioassimilation, and iv) mineralisation (Haider et al., 2019). The first step results in fragmentation of the polymer into smaller particles. Microbial enzymes then in turn catalyse the depolymerisation of the polymer chain into oligomers, dimers, or monomers. These smaller molecules can then be taken up into microbial cells and degraded further (Wood, 2020).

Degradation of any solid polymer can be divided into two types: **bulk erosion and surface erosion** (Albright and Chai, 2021; Haider et al., 2019; Meereboer et al., 2020; Su et al., 2019). In slow bulk degradation processes caused by chemical reactions like hydrolysis, small catalysts (e.g., organic acids) and reagents (here, water) diffuse into polymer systems (Su et al., 2019). This abiotic degradation functions as both bulk and surface degradation and is often used as a pre-treatment to biodegradation. In general, bulk erosion is used for breaking the sample apart into smaller pieces (which enhances the rate of surface erosion) and for molecular weight reduction (Meereboer et al., 2020). The biotic (enzymatic) degradation is mainly at the surface. The reason is that enzymes are relatively large particles and are unable to permeate the structure of polymers, in comparison to smaller chemicals, free radicals etc. (Meereboer et al., 2020; Su et al., 2019). Zumstein et al. (2018) presents an experimental approach to study polymer biodegradation in soils and to assess the key steps involved in this process: microbial polymer colonization, enzymatic depolymerisation on the polymer surface, and microbial uptake and utilization of the released low-molecular weight compounds.

Recently it is also discussed the influence of **fungal enzymes** by biodegradation of plastic material (ECETOC, 2020; Gladfelter et al., 2019; Kang et al., 2019; Sánchez, 2020; Zumstein et al., 2018) in both aquatic (marine) and terrestrial environments. A brief review on the degradation of plastics using enzymes from various sources are given by (Kaushal et al., 2021).

Fungal enzymes play also a major role in the (bio)degradation of **natural polymers**. For example, starch is degraded by glycoside hydrolases, such as  $\alpha$ -amylase,  $\beta$ -amylase, glucoamylase and  $\alpha$ -glucosidase, which are all specialised in hydrolysing  $\alpha$ -glycosidic bonds (Polman et al., 2020; Warren, 1996). In addition, starch can be made more susceptible to biodegradation by gelatinisation (Polman et al., 2020). Fungi and eubacteria form the largest share of the cellulolytic (cellulose-degrading) microorganisms as well (Kögel-Knabner, 2002; Polman et al., 2020). The group of enzymes most responsible for extracellular cellulose degradation are cellulases, which will break the  $\beta$ -glycosidic links (Warren, 1996). For the degradation of lignin many organisms and enzymes are involved, which reflects the complexity of lignin molecules (Polman et al., 2020). For this reason it is obvious that the biodegradation rate is slower.

In addition, the four steps (i) biodeterioration, ii) depolymerisation, iii) bioassimilation, and iv) mineralisation) presented by Haider et al. (2019) are relevant for natural polymers or natural polymeric material as well. Thereby different processes including several enzymatic processes, photolyse/-aging, hydrolyse, as well as bulk and surface erosion will be important to shorten and fragment the polymeric material, and finally mineralize natural polymeric material and substances. An important factor is expected to be the wettability of the material.

### 4.3 Degradation data

Degradation data will usually obtained performing standardized test systems such as the OECD testing guidelines. For polymeric substances availability of studies following these standard biodegradation tests using OECD guidelines are limited. Screening tests such as ready biodegradable test systems according to OECD 301 are rare. Data on simulation studies according to OECD 307, 308 or 309 are not available or at least scarce.

Several studies are available following ISO or ASTM standards, especially for biodegradable synthetic polymers. In ISO standards, reference substance are for example microcrystalline cellulose or ashless cellulose filters and polyethylene (PE) is suggested as negative control. For this reason for these substances many study results may be available.

Non-guideline studies often only provide results on mass loss, or loss of functionality as indication for degradation.

Several compilations of available degradation data have been presented in recent reviews such as

- Kjeldsen et al. (2019) based on data compilation from Emadian et al. (2017)
- Burgstaller et al. (2018), which is a UBA report (cited in EPA network report (EPA network - Interest group on Plastics, 2018))
- Polman et al. (2020) covering natural polymers and modified biopolymers

Some further degradation data from primary literature partly cited in these reviews are available as well (e.g., Arcos-Hernandez et al. (2012); Gómez and Michel (2013); Hashimoto et al. (2002); Kögel-Knabner (2002); Meereboer et al. (2020); Thevenot et al. (2010), etc.)

Further relevant literature data using standardized methods in soil are available from Novamont (Briassoulis et al., 2020; Chinaglia et al., 2018; Pischedda et al., 2019; Tosin et al., 2019) and EU projects (KBBPPS, 2015; Open-Bio, 2016). These studies investigated:

- Starch based (Mater-Bi), PHB, PBSe
- ASTM 5998 and ISO 17556 (mineralization in soil)
- Influence of surface area, temperature

Data for water soluble polymers such as PEGs and some blends are available from Bernhard et al. (2008), Eubeler et al. (2010), Duis et al. (2021).

Direct comparison between different natural and synthetic materials using the same test set-up are available from Gómez and Michel (2013) and McDonough et al. (2017).

An overview of available field/mesocosms studies for soil, freshwater and marine water is given in Burgstaller et al. (2018). This includes for example also information from the Open-Bio project (Open-Bio, 2016; Tosin et al., 2012). As any transformation product or CO<sub>2</sub> cannot be captured, in such test systems mostly only disintegration is measured, followed by mass loss, change of the surface of the particles, or by visual inspection. However, Hennecke et al. (2018) presented a lysimeter study of cationic polyacrylamide copolymers (PAMs) using radiolabelled polymer and thus mass balance was possible. This study shows that there was practically no vertical movement of polymer but a significant reduction of the polymer backbone chain length could be measured over time, which would not be detectable by any of the current ISO standard tests.

Available degradation data (using standardized methods) has been compiled in an excel file (see Annex).

#### 4.3.1 Natural polymers

The (bio)degradation of unmodified, naturally occurring biopolymers in soils has long been a research interest. However, results from OECD testing guidelines (screening and simulation studies) are scarce and mainly information using ISO tests or non-guideline studies are available. Nevertheless some data on natural polymers have been compiled in reviews on bioplastics especially for cellulose and starch. In addition, cellulose (microcrystalline or as ashless filter material) is the reference material for ISO tests.

Overview about degradation pathway and available data for natural polymers (starch, cellulose, lignin) are given by Polman et al. (2020). The review by Kögel-Knabner (2002) contains a table with information on biodegradability (percentage mineralization at different time points up to 28 weeks) of natural substances in soil. Detailed information on the method is missing. Review of the fate of lignin in soil is presented by Thevenot et al. (2010). In addition, some data are available for natural products, e.g., rice hull, coconut coir, wheats straw, walnut shells, etc. (Gómez and Michel, 2013; Kögel-Knabner, 2002; McDonough et al., 2017).

Following results can be summarized for selected natural polymers:

#### **Cellulose**

- Degradation studies in freshwater (activated sludge), seawater or soil available
- Recommended reference substance for ISO tests (validity criterion > 60% in 6 month, results usually higher)
- Relative fast degrading natural polymer
- Some laboratory studies in soil exist with plateau at about 70% mineralization (Gómez and Michel, 2013); other result in higher values (Briassoulis et al., 2020; Chinaglia et al., 2018; Kögel-Knabner, 2002; Martin and Haider, 1986; Pischedda et al., 2019; Tosin et al., 2019)

#### **Starch:**

- Biodegradation asymptotic; large fraction already degrades in soil within 3 days, but can take several weeks to year to be degraded entirely
- In the laboratory starch disappeared (only partly mineralized) within 35 days in soil after incubation (Cheshire et al., 1969; Polman et al., 2020). Other studies show high mineralization (> 80%) in 12 weeks (Kögel-Knabner, 2002; Martin and Haider, 1986).
- Degradation rates may be dependent on concentration; decreasing up to 50% when the starch present is <10% of the soil organic matter (SOM). Low starch concentrations, in combination with low activity of starch degrading organisms could lead to stabilisation of starch in the SOM fraction (German et al., 2011; Polman et al., 2020).

#### **Lignin:**

- The information in the literature leads to slower degradation rates in comparison to cellulose or starch: 19–60% degradation has been observed in laboratory experiments for 13 weeks to 2 years. Information on field studies is given with degradation up to 5 years. Other literature reported that lignin degradation takes years or decades (Polman et al., 2020; Thevenot et al., 2010).
- Various variables and processes such as degradation or mineralization, as well as incorporation into SOM. Lignin turnover in soils could be faster than that of the total SOM. Degradation is related to the nature of vegetation and land-use, but also to the climate and soil characteristics (Thevenot et al., 2010).
- Co-metabolism with easily degradable carbon sources (sufficient energy, nutrients, enzymes)
- The complex structure of lignin makes it recalcitrant to most degradation methods and continues to pose a critical challenge (Datta et al., 2017)

In conclusion, the presented data about biodegradability of natural polymers are varying. The studies are often on composting or field studies in soil, and thus are not according to standardized test systems. As endpoint often mineralization, but also other endpoints such as mass loss. Nevertheless, natural polymers are usually more or less biodegradable. However, rate can vary and some are more difficult to be degraded (e.g. lignin, etc) reflecting the complexity of the substance. Information for all three compartments (soil, aqueous, marine) for the same polymer are scarce; information on degradation in sediment are often lacking.

Natural products has been measured in some test systems as well. In most cases these are less degradable in the test systems used in comparison to cellulose or starch.

The review by Kögel-Knabner (2002) presents for natural materials mineralization data (CO<sub>2</sub> evolved) in soil at different time points up to 28 weeks. Whereas natural substances as glycine, glucose, cellulose or starch resulted in high mineralization (> 80%), other natural material such as walnut wood, almond shells, pine needles resulted in significant lower biodegradation potential (< 60%). Wheat straw shows a mineralization of about 67%, which confirms the lower potential of lignin in comparison to cellulose. Although it seems that it is more a screening test, the kinetic verifies that starch takes longer for the biodegradation in comparison to glucose.

Additional results about natural products are presented below (chapter 4.3.4)

#### 4.3.2 Modified biopolymers

Overview about degradation pathway and available data for modified natural polymers (Thermoplastic starch (TBS), Cellulose acetate (CA), Lignin-based polymers) in comparison to the corresponding natural polymers (starch, cellulose, lignin) are given by Polman et al. (2020). In addition, some degradation data are available for starch blends.

Polman et al. (2020) concluded that especially in TPS, where only a higher level structural change occurs during the bioplastic making process, biodegradation mechanisms and rates are virtually similar. Changes in the biodegradation process are caused by changes in the chemical structure of biopolymers, as occurs during the acetylation of cellulose to produce CA.

In conclusion, modifications of natural polymers can result in intended significant structural and morphological changes, which may have a significant influence on the necessary processes (enzymes) and thus on the biodegradation potential.

#### 4.3.3 Synthetic polymers

Limited information is available using specific standards (ISO, ASTM) for classical polymers such as polyolefins (PE, PP), PS or PET etc. However, several non-guideline studies and field studies are additionally available suggesting that these substances are only marginal biodegradable.

For water soluble polymers, the degradation potential depends on the molecular weight, as shown for polyethyleneglycols (Bernhard et al., 2008; Eubeler, 2010). PEGs are more accessible to biodegradation than Homo- and copolymers of acrylic acid or Polyquaterniums (Duis et al., 2021).

As a good overview about biodegradable synthetic polymers, Burgstaller et al. (2018) summarized following information:

Time of biodegradation strongly depends on the environmental conditions:

- Biodegradable under conditions of “**industrial compostability**“ (58 ± 2 °C, max. 6 month):

- TPS, PHA, PCL: ca. 4-6 weeks

- PLA, PBAT, PBST: ca. 6-9 weeks
- PBS: ca. 21 weeks
- Biodegradable in **soil** (20-28 °C, max. 2 years):
  - TPS, PHA, PBSe, PBSeT, PBAT, PCL: ca. 7-12 month
  - PLA: no degradation after 1 year
- Biodegradable in **fresh water** (20-25 °C, max. 56 days)
  - TPS, PCL, PHA: <56 days
  - PBS, PBSA: ca. 3 month
  - PLA, PBAT: >1,5 years
- Biodegradable in **seawater** (30 °C, max. 6 month)
  - PHA, PCL, TPS, PBSe: <6 month
  - PLA, PBAT: >1,5 years

#### 4.3.4 Examples for comparison of degradation data

In the chapters above, available degradation data for natural and synthetic polymers using standardized methods have been presented. For comparing natural and synthetic polymers, literature data are preferred, which compares the degradation potential using the same method. The number of studies are very limited. Direct comparison between different natural and synthetic materials using the same test set-up are available from Gómez and Michel (2013) and McDonough et al. (2017). In addition, the review by Kögel-Knabner (2002) contains a table with information on biodegradability of natural materials in soil (see above).

##### **McDonough et al., 2017: (modified) OECD 301B, activated sludge**

McDonough et al. (2017) investigated the degradation potential of natural materials and PHBV as a synthetic polymer using a (modified) OECD 301 B test system.

The natural material were applied as microparticles, milled, or as powder. The organic carbon content and the particle size of the different materials have been specified. Some of the natural materials show significantly different degradation kinetics than others. Although the particle size of blueberry seed was larger (100% > 500 µm), the material shows a higher degradation potential than walnut shells with the main particle fraction between 250 – 500 µm, for which negligible mineralization has been observed in this test system. In contrast, the results indicate a very high degradation potential for jojoba wax of a similar particle size as walnut shells.

The synthetic PHBV has been applied in different particle sizes. As a fine powder the biodegradation is similar to the reference substance sodium benzoate, whereas with higher particle sizes the adaptation phase is a slightly prolonged, but the substance is still well biodegradable.

##### **Gomez and Michel, 2013: Biodegradability in soil**

The biodegradation of natural materials in soils was determined based on ASTM 5998-03 by Gómez and Michel (2013). Although the guideline was meanwhile revised, the test results produced some interesting conclusions.

The biodegradation potential of the reference material (cellulose paper) was relatively high (with about 60-70% within 300 days). In contrast using the same test system, coconut coir, rice hull or peat

fibre + wood pulp show only a plateau between 10-40%, which was reached relatively quickly (< 100 days). This indicates that the slow degrading material contains some constituents which are hardly mineralized, and thus will be potentially persistent or incorporated into the biomass.

For PHA a similar maximum biodegradation value within the incubation of 660 days has been observed as for the reference cellulose. The blends of synthetic polyesters with corn starch such as Plastarch have shown a lower biodegradation potential. And the classical polymers such as PP, PS and PET have shown no significant biodegradation.

#### 4.3.5 Summary

The available data indicate that the result are varying on the structural and morphological properties of the polymers. Thereby it doesn't matter if natural, modified, or synthetic. Synthetic polymers are often not biodegradable in sufficient time in terms of the protection goal especially the classical polymers, but can be in some cases ready biodegradable as well, whilst natural polymers are often relatively fast degrading. However, some natural polymeric materials are relatively stable reflecting the complexity of the respective substance and the intended function in nature.

The main data are available on ISO or ASTM methods (mineralization) or using non-guideline studies. The latter studies often only provide results on mass loss, or loss of functionality (indication for degradation). Some data are available for natural polymers such as cellulose or starch, due to the fact that these materials are used as positive reference in the ISO or ASTM test systems. For synthetic polymers data are usually available rather for biodegradable polymers than for clearly expected non-biodegradable polymers. Especially for presumably (very) stable polymers, biodegradation data are rare. Often only non-guideline studies to consider effect of weathering and disintegration are available.



## 5 Comparison natural and synthetic polymers

Both natural and synthetic polymers, are formed by polymerization of small molecules. Similar to synthetic polymers, natural polymers can have significant different structural and morphological descriptors and physico-chemical properties. These are attributed to the polymer's molecular size as well as 2D and 3D structure (linear, branched, crosslinked, and networked polymers). An important factor is e.g. expected to be the wettability of the material. These properties in turn will result in different (bio)degradation kinetics, e.g. some natural polymers are hydrolytically more stable than others.

Natural and synthetic polymers will undergo several processes for biodegradation. In general, the process of polymer (bio)degradation can be divided into four steps: i) biodeterioration, ii) depolymerisation, iii) bioassimilation, and iv) mineralisation (Haider et al., 2019). The first step results in fragmentation of the polymer into smaller pieces. Microbial enzymes then in turn catalyse the depolymerisation of the polymer chain into oligomers, dimers, or monomers. These smaller molecules can be taken up into microbial cells and degraded further (Wood, 2020). Fungal enzymes play a major role in the (bio)degradation of natural polymers. Several enzymatic processes and abiotic processes such as photolysis/-aging, hydrolysis, as well as bulk and surface erosion will be important to shorten and fragment the polymeric material, and finally bring natural polymeric material and substances back in the natural carbon cycle.

Limited number of study results available for natural and synthetic polymers using standardized methods (OECD testing guidelines or polymer specific ISO standards). Literature are preferred, which compares the degradation potential of different polymer sources using the same method.

### **Natural polymers**

- ✓ often only data on weight loss available
- ✓ cellulose and starch biodegradable; reference substance for ISO methods
- ✓ other natural polymers / natural materials potentially more stable reflecting the complexity of the materials (e.g. lignin)
- ✓ fragmentation by weathering; hydrolysis as an important fragmentation process; influence of wettability
- ✓ (fungal) enzymes play an important role in biodegradation

### **Synthetic polymers**

- ✓ only limited number of ISO tests available (mainly for biodegradable polymers)
- ✓ results for blends can overestimate the biodegradation potential if parts are not biodegradable (similar to multi-constituent substances or UVCB)
- ✓ fragmentation by weathering; hydrolysis relevant (e.g. for esters) but also additional processes such as deacetylation
- ✓ enzymes have a major role as well

For both, natural and synthetic polymers, the surface area is important for the biodegradation kinetic. Smaller particles or fragments have a larger surface area, and thus a higher probability to be attacked. For this reason, rate-determining is often but not in all cases the first step, i.e. fragmentation due to physical forces or due to enzymatic processes. In this context weathering parameters (irradiance, temperatures, and relative humidity) are very important for natural and synthetic polymers. If natural polymers are manufactured synthetically with the same structure, the same biodegradability is

expected. In this special case biodegradability is not a question of natural or synthetic “manufacturing”.

Natural polymers are regarded as no concern in the environment. Thus, natural polymers are excluded from the restriction proposal for intentionally added microplastic. As stated in the Annex to the Annex XV report *“Polymers that occur in nature can, by default, be considered to be inherently (bio)degradable in the environment and not contribute to the microplastic concern”* (ECHA, 2020). The available results on biodegradation indicate that some natural polymers might be even ready biodegradable as sufficiently shown for microcrystalline cellulose. However, it is expected that many natural polymers will not be mineralized in sufficient time to meet Annex XIII persistence criteria. The timeframe of the presence in different compartments could be also highly variable depending on the type of polymer and the environmental conditions.

In conclusion, natural polymers are considered inherently biodegradable by default by ECHA (see above) and Annex XIII persistence criteria don't apply to natural polymers. That makes it difficult to use natural polymers as reference for testing of synthetic polymers, because even if the synthetic polymer degrades faster than a natural reference polymer, it might fail the persistency criteria that does not apply to the natural reference polymer. In such case the faster degrading synthetic polymer might be assessed persistent while the natural reference polymer that degrades much slower at the same conditions is not considered an environmental concern.

#### **What can we learn from natural polymers?**

Structures of the natural polymers are often hydrolytically instable, e.g. esters. The hydrolysis is fostered by specific enzymes, so that the microorganism or fungi can use the polymers as energy source or for its biomass. All polymers which are hydrolytically more stable needs additional factors (e.g. specific enzymes) to be degraded in sufficient time in terms of the protection goal. If the effort to get this energy with specific enzymes is unfavourable, for example as long as other sources are available, biodegradation of the polymer will slow down.

Biodegradation is a stepwise process. After biotic and/or abiotic fragmentation, conversion into oligomers, dimers, or monomers by depolymerisation occurs, which will be degraded further by microorganisms and fungi.

In the environment natural polymers (biopolymers) and/or their transformation products will be mostly found in the top layer of soil. The absolute amount is a result of the equilibrium between emission to the soil and the degradation processes. The emission depends on the vegetation, and degradation potential is related to the nature of vegetation, climate and land-use as well. Adapted microorganism, i.e. bacteria and fungi will be found depending on the sources of energy, the climate and soil characteristics.

For natural polymeric materials such as wood, the degradation will be longer than for the polymer (substance) itself such as cellulose or lignin. The reason is the unfavourable surface to volume ratio and thus limited accessibility to be attacked by UV, water, temperature, or microorganism. As soon as the natural materials are fragmented to small pieces (e.g. chipped wood, sawdust etc.) the degradation time will decrease. However, wood and even leaves can exist in forest for years after a tree has died in dry conditions and it is typically removed by fungal degradation. Furthermore even chipped wood will exceed ECHA persistence criteria. This is due to the intended function of wood in nature as skeletal material. Rapid degradation would not allow trees to grow as they are found in nature. Lignin even protects woody cell walls against microbial attack (Kögel-Knabner 2002).

This is backed up by the literature on comparison studies of milled natural material with synthetic polymers (see chapter 4.3.4) which indicate that in some cases the natural polymer and material will be ultimately biodegradable, and in other cases not. Often slow degrading material contains some

constituents which are hardly mineralized, and thus will be potentially persistent or incorporated into the biomass.

## 6 Conclusion

Several types of polymers are on the market and different possibilities exist to categorize these polymers. Besides the grouping based on structural, morphological properties, or physico-chemical properties, the polymers could be grouped based on the source: natural polymers (or biopolymers), modified biopolymers and synthetic polymers. Another option is to (sub)group the synthetic polymers into bio-based and fossil-based polymers. Finally, the polymers could be grouped into biodegradable and not biodegradable. Thereby grouping as bioplastic is misleading. Bioplastics are bio-based or biodegradable or both (European Bioplastics, 2018). For this reason not all bioplastic are biodegradable per definition.

Polymers exist in nature as well. These so called natural polymers (or biopolymers) include natural rubber, cellulose, hemicellulose, starch, lignin, chitin, cutin. Sometimes natural polymers are used as food additives such as glucomannan, agar, pectin, inulin, rosin, guar gum, locust bean gum, gum acacia, karaya gum, gum tragacanth, alginates, carageenans, psyllium and xanthum gum. Natural polymers are often polysaccharides or its derivatives with weak  $\alpha$ -glycosidic bonds or stronger  $\beta$ -glycosidic linkages, but could have also different structural linkages and a high variety of molecular weights, i.e. more complex polymers are available such as lignin. The natural polymers could exist crystalline, semi-crystalline or amorphous, are often insoluble, and can be hydrophilic but also hydrophobic. Thus, different structural and morphological descriptors and physico-chemical properties can be assigned. Based on these descriptors and properties, some natural polymers are expected to be hydrolytically more stable than others. It is obvious that they will have different potential for (bio)degradation.

Natural and synthetic polymers undergo several processes for biodegradation. In general, the process of polymer (bio)degradation can be divided into four steps: i) biodeterioration, ii) depolymerisation, iii) bioassimilation, and iv) mineralisation (Haider et al., 2019).

Large number of studies have been carried out to investigate biodegradation of polymeric substances and material using non-guideline methods. These studies often only provide results on mass loss, or loss of functionality, which both are indeed an indication for degradation. In recent years, several standards have been developed to consider the specific needs of testing plastic and polymeric material. These are mainly ISO or ASTM guidelines, which are often very similar. Thereby guidelines for measurement of the biodegradation of plastic material include different compartments, e.g. aqueous medium/surface water, marine water and sediment, and soil. The ISO (and ASTM) test guidelines are usually following the degradation via indirect sum parameters such as  $O_2$  consumption or  $CO_2$  evolution(=mineralization). Relative high concentration of substance is used and incubation at temperatures between 15 and 28 °C. Testing reference material is prescribed as validation criteria, e.g. cellulose is recommended in same shape and size comparable to that of the test material. As result, these standards provide the degree of mineralization at the plateaus or after a specific time; in addition, ISO 23517 and ISO 22403 give a benchmarking to reference material. These standards can be regarded as similar to screening test systems, especially enhanced test systems, under the standard persistence assessment scheme. ISO methods (or ASTM) are also available to consider the weathering processes, or real field conditions, and frameworks to combine weathering and biodegradation. Some standards are available with further metrics on degradation rate such as erosion rate, mass loss rate (mass or surface area), loss of tensile properties.

Based on these standards, the available information and understanding of biodegradation of polymeric substances and materials is increasing. Some data are available for natural polymers such as cellulose or starch, due to the fact that these materials are used as positive reference in the ISO or ASTM test systems. For synthetic polymers data are usually available rather for biodegradable polymers than for clearly expected non-biodegradable polymers. For the latter polymers, often only non-guideline

studies are available to consider effect of weathering and disintegration. Especially for (very) stable polymers, biodegradation data are rare.

The main message on data availability can be summarized as follows:

- ✓ Metrics used for available (bio)degradation data (laboratory as well as mesocosm/field tests): respirometry, mass loss or specific surface degradation rate (SSDR), tensile test.
- ✓ Standard methods on biodegradation of polymers are usually based on mineralization (respirometry) only
- ✓ Limited number of studies according to ISO methods (soil or water), very limited data for sediment
- ✓ Data with simulation studies are rare

The available data indicate that the result are varying on the structural and morphological properties of the polymers. Thereby it doesn't matter if the polymer origin is natural, modified natural, or synthetic. Synthetic polymers are often not biodegradable in short time especially the classical polymers, but can be in some cases readily biodegradable as well, whilst natural polymers are often relatively fast degrading. However, some natural polymeric materials are very stable against biodegradation reflecting the complexity of natural polymers and its function in natural systems.

The results of actual available screening tests indicate that many natural polymers must be regarded as being not readily biodegradable or even not inherently biodegradable, in the sense of an inherent biodegradation test (OECD 302). Indeed, current simulation tests are missing and thus the ability to come to a final conclusion on persistency for such materials. However, there is no doubt that many natural polymeric materials will fail the persistence trigger values for PBT assessment given in Annex XIII of the REACH regulation (EC, 2011). It is the intention of nature to form resilient materials for example for protection or skeletal constructions of organisms. Natural polymers are not considered an environmental concern and they are not subject to persistency assessment. Additional properties such as the emission pattern, (bio)accessibility or bioavailability, and a host of real life factors which are not currently included in (bio)degradation studies (e.g. light, temperature extremes, physical damage, ingestion, inadvertent exclusion of competent fungal organisms, etc.) play a major role in the fate of these natural polymers.

The conclusion which can be drawn is that, applying the REACH Annex XIII criteria many natural polymers have to be regarded as P/vP. But those criteria don't apply and they are considered no concern for the environment for good reasons. But this needs to be recognized when assessing synthetic polymers, many of which would fulfil the P/vP criteria as well. For such synthetic polymers it would be important to establish polymer specific criteria to enable an adequate hazard assessment.

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## Annex: Degradation data

Available degradation data (using standardized methods) has been compiled in an excel file.