

Final Report

WP2C – Framework on persistence assessment for Polymers and Microplastics

Cefic-LRI ECO52 project

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Acronyms and Abbreviations

AE	Alcohol ethoxylates
DegT50	Degradation time 50
DT50	Disappearance time 50
EDPL	European Polymer Dispersion and Latex Association
IAS	Intentionally added substances
ISO	International Organization for Standardization
ITS	Integrated Testing Strategy
IUPAC	International Union of Pure and Applied Chemistry
MP	Microplastic
NIAS	Non-intentionally added substances
OECD	Organization for Economic Co-operation and Development
P	persistent
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 are a group of substances which have previously been considered exempt from registration and evaluation under the EU REACH regulations “*since polymer molecules are generally regarded as representing a low concern due to their high molecular weight*” (ECHA, 2012). However, polymers may still be subject to authorisation and restriction. In the future, polymers potentially require registration under REACH, and thus environmental hazard and fate assessment including persistence assessment.

The term polymer can encompass a very diverse range of products which needs to be defined more precisely before proposing any ‘polymer’ persistence assessment approach. Using the ECHA polymer definition (ECHA, 2012), polymers comprise such diverse substances as insoluble solid ‘plastic’ polymers, liquid polymers, soluble polymers, smaller oligomeric polymers (e.g. surfactants), etc. In addition, we have to differentiate between polymeric substances and plastic materials or articles. Moreover, polymers are a class of substances which are often designed to be as much as possible stable during a relatively long use phase in articles. Specific physico-chemical properties of polymers may result in specific technical limitations for the applicability of the standard guidelines, and may affect their fate in the environment. For example, water soluble, poorly soluble, and water insoluble/particulate polymers will show quite different fate behavior (ECETOC, 2020).

Generally, the OECD TG 300 series of tests will be used to assess the fate of substances in the environment. However, most of the OECD TG 300 test methods were originally developed for well-defined low molecular weight (LMW) substances that are typically mono-constituent, water-soluble and uniformly dispersed within the aqueous solution, and the corresponding ring trials did not include polymers (ECETOC, 2020). For this reason, the assessment of the environmental hazard and fate properties of polymers is associated with considerable challenges that go beyond the assessment of individual substances. Certain existing frameworks for safety assessment are challenging the assessment process for polymers and demonstrate the need for adaption. Knowledge gaps for polymer hazard and risk assessment have been identified in the ECETOC TR No. 133-1 (ECETOC, 2019). Many of the identified knowledge gaps relate to the applicability of standard analytical tools, test methods and in silico models (ECETOC, 2020). Four major challenges have been identified for assessing polymer biodegradation by Albright and Chai (2021): (1) a lack of standardization in polymer biodegradation testing, (2) the long durations required in biodegradation testing, (3) demanding analytical methods, and (4) a lack of a framework for assessing the overall persistence of polymers.

A special case is the discussion about persistence assessment of microplastics. Microplastics are a subset of polymers defined by a particular physical form. They may be primary microplastics, i.e. intentionally added to products, or secondary microplastics, i.e. formed from abrasion of articles. In the EU the restriction of intentionally added microplastic is proposed unless a polymer can be shown to be biodegradable.

Overall, polymers are identified as posing challenges to their persistence assessment under the standard framework, or are outside its applicability domain.

In this report, the focus has been on how to obtain relevant and credible information to assess the environmental persistence of polymers (not plastic materials or articles). Finally, a framework (including suitable workflows/decision trees) proposed to support the persistence assessment of polymers (and microplastics) in a weight of evidence approach.

In this context it is also important to have a view on the definition of persistence and the protection goal. Persistence as assessed is a classification. The main concerns associated with highly persistent substances is their potential to lead to widespread, long-lasting, and increasing contamination, increasing probabilities that known and unknown effects occur, and it will be challenging to reverse

the chemical contamination and therefore the effects (Cousins et al., 2019). Especially the uncertainties related to yet unknown long-term effects is maybe critical. Thus, from a safety perspective the protection goal will be to avoid long-term and poorly reversible accumulation of the chemicals in the environment, especially if these substances are also considered to be bioaccumulative, and possibly toxic. In Europe, according to Section 4 of Annex I to the REACH Regulation (EC 1907/2006) a conventional hazard assessment of the long-term effects and the estimation of the long-term exposure cannot be carried out with sufficient reliability for substances satisfying the PBT and vPvB criteria in Annex XIII (EC, 2006). The persistence criteria given in Annex XIII of the REACH regulation (EC 253/2011) are defining the persistence within the PBT assessment under REACH (EC, 2011). This annex requires a weight-of-evidence (WoE) approach considering information on simulation testing (or screening) for different compartments based on standard protocols. Additional sources of information such as field studies or monitoring studies under the auspices of the EU Water Framework Directive 2000/60/EC might help to identify substances of potential concern. The overall persistence (Pov) may represent an alternative approach for persistence assessment to meet the protection goal (Redman et al., 2021). Alternative endpoints have also been discussed in WP3 of this Eco 52 project. Please note, a substance could be classified as persistent based on the criteria given above, and at the same time be ultimately degradable in the environment. For example if degradation is not fast enough or takes place only in specific compartments and under specific conditions.

Particularly for polymers, other factors need to be taken into account to meet the protection goal, e.g. resource efficiency, sustainability, or product life. Moreover, their lack of bioavailability to degrading organisms is a common characteristic linking polymers with difficult test substances (WP2A). In the case of polymers, it is due to their physical form and/or very large molecular size which prevents microorganisms from accessing large parts of the material. For this reason the bioavailability has a significant impact on biodegradation of polymers and can be considered a confounding factor where the intrinsic biodegradation potential is intended to be tested. The standardised persistence assessment is additionally complicated by the complex and variable nature of different classes of polymers. In recent years several standard protocols for biodegradability testing have been adapted or developed with focus on polymers and (micro-)plastic materials (ASTM and ISO standards).

Polymers exist also in nature, which comprise for example, cellulose, chitin, protein, carbohydrates such as starches etc. Also for natural polymers the timeframe of biodegradation could be highly variable depending on the conditions. Similarities and differences between natural and synthetic polymers are given as a separate report (WP4).

In this report, important aspects of the proposed framework for persistence assessment of polymers are influencing parameters such as bioavailability, and the understanding of biodegradation potential of natural in comparison to synthetic polymers. The framework should give insight how the existing criteria on persistence assessment for single substances in the PBT assessment under REACH can be used, interpreted or have to be adapted for polymers to avoid long-term presence and accumulation in the environment.

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 Guiding principles for Persistence assessment of Polymers

2.1 Polymer Definition

For the definition of polymers, we have to differentiate between the polymer itself as a polymeric substance, and the polymer product or plastic as a material or the finished article.

According to ISO 472 (ISO, 2013), *“plastic is a material which contains as an essential ingredient a high polymer and which, at some stage in its processing into finished products, can be shaped by flow. Plastics product is any material or combination of materials, semi-finished or finished product that is within the scope of ISO/TC 61, Plastics.”*

The definition of polymers by IUPAC¹ is: *“Substances composed of macromolecules, very large molecules with molecular weights ranging from a few thousand to as high as millions of grams/mole.”*

OECD² 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.”*

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 (see definition below); 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.*
- *A "monomer unit" means the reacted form of a monomer substance in a polymer (for the identification of the monomeric unit(s) in the chemical structure of the polymer the mechanism of polymer formation may, for instance, be taken into consideration).*
- *A "sequence" is a continuous string of monomer units within the molecule that are covalently bonded to one another and are uninterrupted by units other than monomer units. This continuous string of monomer units can possibly follow any network within the polymer structure.*
- *Other reactant refers to a molecule that can be linked to one or more sequences of monomer units but which cannot be regarded as a monomer under the relevant reaction conditions used for the polymer formation process.*

A polymer, as any other substance defined in Article 3(1), can also contain additives necessary to preserve the stability of the polymer and impurities deriving from the manufacturing process. These

¹ <https://iupac.org/polymer-edu/what-are-polymers>

² <http://www.oecd.org/env/ehs/oecddefinitionofpolymer.htm>

stabilisers and impurities are considered to be part of the substance and do not have to be registered separately.

Substances may also be added to improve the performance of the polymer even though they are not necessary for preserving the stability of the polymer. Indeed, substances are commonly added to a polymer for the purpose of adjusting or improving the appearance and/or the physico-chemical properties of the polymeric material. Examples of such substances include pigments, lubricants, thickeners, antistatic agents, antifogging agents, nucleating agents and flame retardants. When a polymeric material contains such substances it should be considered as a mixture or an article.”

Part of the polymer, i.e. **substance**

- (a) additives such as stabilizers
- (b) impurities such as catalysts residues
- (c) unreacted monomers

Part of the "material" i.e. **mixture/article**

other additives such as pigments, lubricants, thickeners, antistatic agents, antifogging agents, nucleating agents and flame retardants

Based on this definition, a polymer as a substance is a mixture of multiple components, where the components are very similar (macro)molecules with different chain length. For this reason there is an analogy between polymers and multiconstituent substances or UVCB (substances of unknown or variable composition, complex reaction products or biological materials), and thus similar issues with regard to degradation evaluation.

There are four basic polymer structures (and probably many variations of these): linear, branched, crosslinked, and networked polymers. For this reason, we have also to consider the three dimensional structures of polymers in any degradation evaluation and polymer persistence assessment. In this context we can also have a detailed view on the dimensions of polymers. Typically polymers are < 1 Mio Daltons (Da), but higher molecular weights are also possible, for example Ultra-high-molecular-weight polyethylene (UHMWPE) is available with molecular weights of 2-6 million Daltons. Typically, a linear polymer with a molar mass of 1 million Da consist of less than 10000 repeat units. This corresponds to a length of a completely stretched chain of < 20000 atoms, and thus a length of < 2.7 μm (= 27000 Å). However, often polymers will have an even smaller dimension as they adopt a coil conformation.

2.2 Microplastic Definition

Microplastic (MP) can roughly be divided into primary microplastic and secondary microplastic.

Primary microplastic (primary MP) are industrially manufactured for example as microbeads of different sizes, and intentionally added to (consumer) products such as personal care products. These primary MP enter the environment during manufacture, transportation and use (Andrady, 2017).

Secondary microplastic (secondary MP) will be formed by fragmentation from larger plastic articles. The likely predominant source of secondary microplastic in marine environment is the weathering breakdown of plastic litter (Andrady, 2017). Further important source of secondary MP is the abrasion

of tires (Sommer et al., 2018). Other MP sources includes textile fibre fragments and post-use agricultural mulch films (Andrady, 2017).

In the ECHA Committees for Risk Assessment (RAC) opinion for the restriction of intentionally added microplastic (ECHA, 2020), microplastic is defined as: *“microplastic’ means particles containing solid polymer, to which additives or other substances may have been added, and where $\geq 1\%$ w/w of particles have (i) all dimensions $\leq 5\text{mm}$, or (ii) a length of $\leq 15\text{mm}$ and length to diameter ratio of > 3 .”*

From this definition it is clear that polymers that are not solid particles are not ‘microplastic’.

The lower dimension of the particles has been discussed during the preparation of the final opinion. The primary suggestion of the Annex XV dossier submitter (ECHA) was to define as ‘microplastic’ all dimension from $1\text{ nm} \leq x \leq 5\text{ mm}$, which has been revised in the meantime to $100\text{ nm} \leq x \leq 5\text{ mm}$. However, RAC concluded that these size limits could exclude relevant nanoscale (nanoplastic) particles from the scope of the proposed restriction, and thus there is no clear scientific basis for determining a specific lower size limit in terms of hazard. For this reason they consider it appropriate to define microplastic without the use of a lower size limit.

However, it is also mentioned that the nanoscale is on a molecular level. For example, a length of 1 nm is equivalent to the length of three water molecules or a single molecule of octane. On this basis, a particle of 1 nm would be unlikely to be a solid polymer, and a particle would be unlikely to be a REACH polymer if it was $< 50\text{ nm}$ in size (ECHA, 2020).

2.3 Types of Polymers

Different types of polymer products are on the market. The complex and variable nature of these different classes or types of polymers creates difficulties in developing a standardised approach to evaluate degradation potential and assess the persistence of polymers. It is considered essential to identify and ideally group polymers into different classes/categories and propose approaches suitable for each category. For different types of polymer products, different structural and/or morphological descriptors as well as physico-chemical properties are expected to be relevant (ECETOC, 2019, 2020). The following section will give an overview about the different types of polymers and potential grouping.

Generally, polymeric substances and materials can be characterized 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).

In addition, as mentioned above polymers usually consist of (macro)molecules, with different polymeric structures (linear, branched, crosslinked, and networked polymers). Different physical state of the polymers exist such as liquid, close to liquids, resins or often solid. Solid material can have crystalline, partly crystalline but also amorphous regions, and the different degrees of crystallinity and wettability will have an impact on their properties. For example, the introduction of 3-hydroxyvalerate in Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) results in a greater amorphous region (Meereboer et al., 2020). Other molecular parameters include ratios of monomers which may affect crystallinity, e.g. urea formaldehyde resins ((Park and Jeong, 2011)). The F/U molar ratio is linked with the degree of branching and the number of methylol groups. For this reason, 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.). For example, 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). For insoluble plastic materials these have a wide range of densities (0.01 to 2.3 g/cm³ (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.

Polymers can also be grouped on their “behaviour”. ‘Thermoplastic’ materials are capable of being softened repeatedly by heating and hardened by cooling through a temperature range characteristic of the plastic and, in the softened state, of being shaped by flow repeatedly into articles by moulding, extrusion or forming (ISO, 2013). Typical thermoplastics are polyethylene [PE], polypropylene [PP], poly(vinyl chloride) [PVC], polystyrene [PS] and poly(ethylene terephthalate) [PET]. The polymer chains are linked by intermolecular forces. Post-use thermoplastics can be readily recycled by re-melting them to form other products. In contrast, ‘Thermoset’ are plastic which, when cured by heat or other means, changes into a substantially infusible and insoluble product (ISO, 2013). By curing the crosslinking gives the polymer a permanent 3D structure. Typical thermosets are for example Vulcanized rubber, Bakelit, Duroplast, Urea-Formaldehyde resins, Polyurethane. A classification of synthetic polymers encountered in marine debris and in MPs with examples of debris in each category is given in Andradý (2017). From this it can be concluded that both thermoplastic and thermoset plastic contribute to ocean MPs.

Finally, polymers can roughly be divided into fossil-based and biobased polymers, i.e. polymers for which bioresources have been used for manufacturing. Bioplastics are biobased, biodegradable or both (European Bioplastics, 2018), which can be illustrated in a material coordinate system of plastics as given in Figure 1.

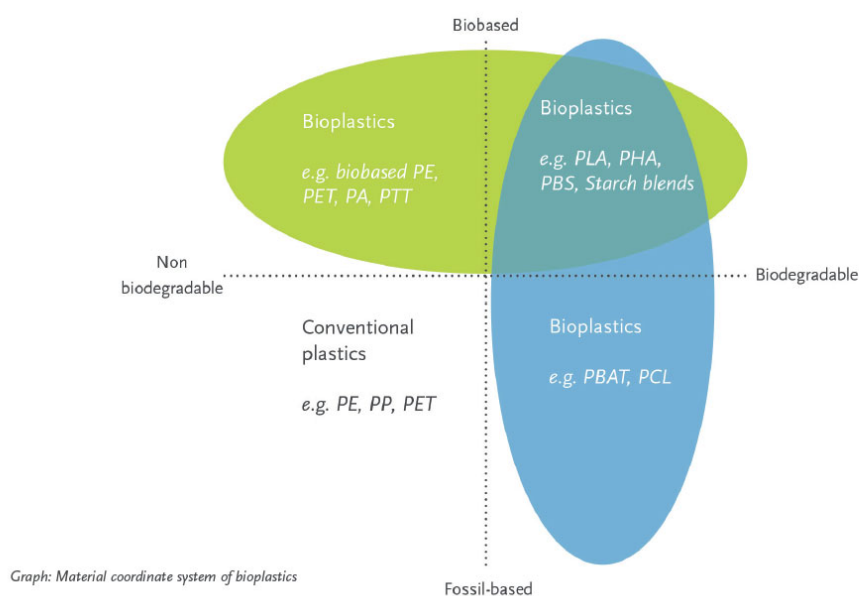


Figure 1: Material coordinate system of plastics according to European Bioplastics (2018)

An additional grouping will be on natural polymers, semi-synthetic polymers and synthetic polymers. Natural polymers (or also named biopolymers) are polymers which exist and are made in nature (e.g. cellulose, hemicellulose, glucomannan, agar, starch, pectin, inulin, rosin, guar gum, locust bean gum, gum acacia, karaya gum, gum tragacanth, chitin, alginates, carageenans, psyllium and xanthum gum,

etc.). These substances can be assigned to the biobased polymers or often even to the group of biodegradable bioplastics. Polymers that occur in nature can, by default, be considered to be inherently (bio)degradable in the environment and do not contribute to the microplastic concern (ECHA, 2020).

Overview of different groups of polymers and case studies is given by ECETOC (2021), identifying sets of key parameters for the respective types of polymers, which have to be established on a case-by-case basis. In addition, grouping of polymers was recently discussed for registration purposes as well. Using alcohol ethoxylates (AE) as an example the “3-layer approach” has been described to get a group of polymers with hazard similarity taking into account chemical nature, physico-chemical / structural properties, and hazard properties (CESIO, 2021). AEs are a very widely used class of non-ionic surfactants and commonly derived from linear or branched primary alcohols with alkyl chain lengths ranging from C8-22 and ethylene oxide typically ranging from 1 to 50 units (similar to UVCB substance with basic structure Cx-yEO_n). Please note that from a regulatory point of view AEs with $n < 2.5$ are REACH registered substances, and not polymers.

Specific case of a group of potentially polymeric substances are paraformaldehyde and reaction products of formaldehyde with other monomers. For example, amino resins are produced by polymerisation of formaldehyde with either one or a mixture of other monomers, the most common being urea and melamine. The products are complex mixtures containing low molecular weight polymeric precursors, residual monomers and a solvent that is either water or an alcohol (Formacare, 2021).

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). All these properties are mostly independent from each other, and thus it is necessary to identify those properties, that make a difference for degradation potential. Due to the high variability of different polymer types it is expected that one approach for assessing persistence will not cover all different polymer types, and thus is not sufficient. This indicates that a case by case decisions on the applied approach for single polymer types or justified appropriate grouping of polymers may be advisable, which should be part of the weight of evidence.

2.4 Terminology of Fate, Degradation and Persistence

In the literature there are several definitions available about terms which are relevant to assess persistence. An overview is given in the following.

From a general perspective, ‘environmental persistence’ can be tentatively defined as the propensity for a chemical to remain in the environment before being transformed by chemical and/or biological processes in a particular environmental compartment (Redman et al., 2021). No clear scientific consensus exists about how long a chemical must persist in the environment for it to be considered of concern. For this several additional aspects have to be considered such as inertness, hazard, probability of unknown effects of long time low concentrations.

According to **ISO 472** (ISO, 2013),

- **Biodegradation** is the degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of a material.
- **Degradation** is the irreversible process leading to a significant change in the structure of a material, typically characterized by a change of properties (e.g. integrity, molecular mass or structure, mechanical strength) and/or by fragmentation, affected by environmental conditions, proceeding over a period of time and comprising one or more steps.
- **Disintegration** is the physical breakdown of a material into small fragments.

Definition of terms associated with persistence and degradation is given in **REACH guidance R.7b** (ECHA, 2017a), and an extract is given in Table 1.

Table 1: Glossary of terms associated with degradation according to Table R.7.9—1 of REACH guidance R.7b (ECHA, 2017a)

Term	Definition
Persistence	A substance that resists degradation processes and is present in the environment for a long time. Specific criteria have been established in Persistent Organic Pollutant (POP) protocols, in the TGD and in REACH (PBT/vPvB; see sections 1.1.1 and 1.2.1 of Annex XIII to REACH). In the latter persistent (P) and very persistent (vP) refers to substances that have degradation half-lives above certain trigger values in surface water, sediment or soil.
Fate	Distribution of a substance in various environmental compartments (e.g. soil or sediment, water, air, biota) as a result of transport, partitioning, transformation, and degradation.
Biodegradation	The biologically mediated degradation or transformation of substances usually carried out by microorganisms.
Abiotic degradation	Degradation mediated through processes other than biodegradation such as hydrolysis, photolysis and interactions with other substances (e.g. oxidation). Abiotic degradation studies typically provide a measure of primary degradation.
Degradation rate constant	Typically a first order or pseudo first order kinetic rate constant, k (d ⁻¹), which indicates the rate of the degradation processes. However, depending upon the ratio of the substance to degrader biomass, the rate constants may be Monod constants reflecting growth processes.
Half-life, $t_{1/2}$	Term used to characterise the rate of a first or pseudo-first order reaction. It is the time interval that corresponds to a concentration decrease by a factor 2. The half-life and the degradation rate constant are related by the equation $t_{1/2} = -\ln 2/k$. Half-lives are usually expressed in hours or days and can be assigned to either primary degradation or ultimate biodegradation (mineralisation).
DT50	(Disappearance Time 50) is the empirically measured time within which the initial concentration of the test substance is reduced by 50%. It should be stated whether the DT50 refers to primary degradation or mineralisation (ultimate biodegradation)

Based on this definition given in REACH guidance R.7b (see Table 1), persistence is defined by the degradation half-lives given in Annex XIII to REACH (see **Fehler! Ungültiger Eigenverweis auf Textmarke.**). Consequently, a substance could be ultimately degradable, but can still be regarded as persistent due to degradation half-lives being above the trigger values. For this reason, general (bio)degradability of a substance cannot be equated with non-persistence without considering the rate of degradation (DegT50 = half-life). And, persistent cannot be equated with long-term presence in the environment. Even substances with an overall persistence half-life near 180 d, will be removed within a few years after emission has been ceased.

Table 2: Persistence (P/vP) criteria according to Annex XIII and related simulation tests according to REACH guidance R.11 (ECHA, 2017b)

According to REACH, Annex XIII, a substance fulfils the P criterion when:	According to REACH, Annex XIII, a substance fulfils the vP criterion when:	Biodegradation simulation tests from which relevant data may be obtained include:
The degradation half-life in marine water is higher than 60 days, or The degradation half-life in fresh- or estuarine water is higher than 40 days, or	The degradation half-life in marine, fresh- or estuarine water is higher than 60 days, or	OECD TG 309: Simulation test – aerobic mineralisation in surface water
The degradation half-life in marine sediment is higher than 180 days, or The degradation half-life in fresh- or estuarine water sediment is higher than 120 days, or	The degradation half-life in marine, fresh- or estuarine sediment is higher than 180 days, or	OECD TG 308: Aerobic and anaerobic transformation in aquatic sediment systems
The degradation half-life in soil is higher than 120 days	The degradation half-life in soil is higher than 180 days	OECD TG 307: Aerobic and anaerobic transformation in soil

Furthermore, it is necessary to clarify the terms transfer, removal, abiotic degradation, and primary degradation with regard to persistence assessment.

According to the R.11 guidance (ECHA, 2017b), *“with regard to persistence, it is insufficient to consider removal alone where this may simply represent the transfer of a substance from one environmental compartment to another (e.g. from the water phase to the sediment). Degradation may be biotic and/or abiotic (e.g. hydrolysis) and result in complete mineralisation, or simply in the transformation of the parent substance (primary degradation). Where only primary degradation is observed, it is necessary to identify the degradation products and to assess whether they possess PBT/vPvB properties. In addition to the substance intrinsic properties, its transformation and/or degradation is dependent on the surrounding environment.”* It is additionally mentioned that *“Data derived from other abiotic studies (e.g. photodegradation, oxidation, reduction) cannot be used on their own within persistence assessment, but may be used as part of a Weight-of-Evidence approach. Due to the large variation in the light available in different environmental compartments, the use of photolysis data is not generally recognised for persistence assessment”* (ECHA, 2017b).

It is also self-evident, that the criteria specified in Annex XIII are valid for (organic) substances. However, their applicability to particulate materials, and to the microplastic concern specifically, is less certain (ECHA, 2020). Single (liquid) substances consisting of relatively small and/or water soluble molecules exist at environmental relevant concentrations usually as single molecules not as an agglomerate. In this case the bioavailability and thus degradation potential is usually not limited due

to mass density distribution. In contrast, molecules of solid material or finished (solid) articles are not evenly distributed in the environmental compartments. For degradation, these materials have to be eroded and probably fragmented to get sufficient bioavailability of the complete mass, and this step could be the limiting process. In this case the total degradation time for the whole material could be significantly longer than for the actual substance.

In this context it is also of interest to discuss persistence, degradation and distribution with regard to particles. Generally, particles can be categorized based on their size and shape (e.g. macro, meso, micro or nano, but also potentially as fibres). These particles can be degraded by surface erosion or bulk erosion. During surface erosion the size of the particles will change but not the number of the particles. In contrast during bulk erosion the number of particles will change but not the size (and mass) of the particles. Both will result in a loss of material in the environment, which can be considered as (bio)degradation. This is in agreement with the information available in the regulation and guidance about the test requirements to evaluate degradation of nanoforms. According to the REACH regulation column 2 (EC, 2006): *“For nanoforms that are not soluble, nor have high dissolution rate, such test(s) shall consider morphological transformation (e.g. irreversible changes in particle size, shape and surface properties, loss of coating), chemical transformation (e.g. oxidation, reduction) and other abiotic degradation (e.g. photolysis).”*

Overall, degradation processes of (water soluble or insoluble) polymers and of particles, materials or finished articles are expected to be significantly different to simple liquid low molecular substances. Thus it is questionable if their degradation rate and thus their expected long-term presence in the environment can be compared directly to the criteria for persistence given in Annex XIII. In view of the authors of this report, the criteria of degradation rate (compartment specific half-life) principally takes into account that for single substances the degradation results in an irreversible significant change (increase or decrease) in the structure of the substance, which is typically characterized by a change of relevant properties of the mass (reactivity, toxicity, etc). The process of primary degradation involves usually the making and breaking of covalent bonds. If primary degradation is observed the transformation products have to be evaluated for persistence assessment. By extrapolating this to solid materials such as polymers, transformation processes of particles which result in an irreversible significant change of the structure and surface, and thus potential of toxic effects, might be assumed to be degradation in the sense of persistence assessment. However, in this case each transformation product, i.e. eroded particle, has to be assessed for persistence (and B and T) as well. Only mineralization completely removes the polymer from the environment and is therefore of value from an ecological standpoint (Andrady, 2017).

In conclusion, in environmental regulations half-lives are used as assessment criteria to define persistence of substances. It is challenging to extrapolate these criteria to polymers or water insoluble substances and particles. Finished (solid) articles are not evenly distributed in the environmental compartments, and thus increasing the bioavailability is the limiting process necessary for biodegradation of the actual polymeric substance. Persistence assessment should be directed rather on the substance than on materials or articles.

3 Environmental fate of Polymers

As previously mentioned polymers are a diverse substance group with a wide range of types and properties. The polymers can roughly be grouped into solid, liquid, semi-liquid and resin-type polymers. Some of these polymers are water soluble or form micelles other are not water soluble. Many of these properties will be intrinsically linked to their environmental fate.

3.1 Distribution and Degradation pathway

It is obvious that the different polymer types (solid, liquid, resins, water soluble or non water soluble) will distribute differently in the environment and different degradation processes may be important.

It is assumed that water soluble polymers will behave similar to traditional water-soluble substances. However, the high molecular weight as well as the orientation of the structures can have a significant influence on the degradation potential and kinetic. As polymers are mixtures of different molecular species, and thus can contain a huge number of individual components, that are, however, variations of the same basic structure, it is also clear that total degradation is the combination of all individual degradation kinetics. For liquid non water soluble polymers, the distribution and fate in the environment may be similar as for other non water soluble organic substances. Depending on the concentrations in the environmental matrices, different phases may be formed, which have a significant influence on the bioavailability and thus degradation potential.

In addition, polymers are often present as solid material, which can have crystalline, partly crystalline but also amorphous regions, and the different degrees of crystallinity and wettability will have an impact on their environmental fate and behaviour. As mentioned above, degradation of solid particles can probably not equate solely to the definition of degradation of substances which are present as individual molecules. Resin type polymers are highly viscous or even solid, so that the homogeneous distribution in water matrices is hampered, and thus the expectations for the fate is that similar processes are crucial as for solid materials. Finally, semi liquid polymers may behave similar to solids or liquids.

By comparison to simple single substances, main differences in the fate and degradation processes are expected for solid materials. For this reason in the following focus is on the behavior of particulate polymer substances. However, some processes discussed below may also be relevant for liquid or resin type polymers due to the high molecular weight which is characteristic to all polymeric 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).

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 as for all small 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.”* In addition and complementary to this, if it can be shown that disintegration will result in biodegradable non-persistent particles, fragmentation may be considered as a first step of plastic removal.

One key point is that the starting point of polymer fragmentation and degradation is often photolysis and/or hydrolysis. However, the use of photolysis data is not generally recognised for persistence assessment (ECHA, 2017b).

Photolysis (UV radiation) is the most important process of weathering (Andrady, 2017). In this process the polymer or the additives such as the stabiliser will 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 addition, 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 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 depolymerization 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 in the biodegradation process 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.

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). This is probably radically different from the assessment of degradation of chemicals for which the OECD 300 series of tests has been designed.

In conclusion, when assessing polymer persistence the whole degradation process (fragmentation, biodeterioration, depolymerisation, bioassimilation, mineralization) needs to be considered in a weight of evidence approach. To be consistent with the persistence assessment of single substances, transformation products (smaller particles/fragments, released substances, and particles with altered surface) may be evaluated if they are not persistent as well.

3.2 Standard test protocols for Polymers

Recommended OECD guidelines for measurement of biodegradability are usually developed to assess small, soluble molecules, and not explicitly developed to measure the biodegradation of polymers and UVCBs. Polymers are usually not a part of interlaboratory validation studies nor are many polymers used as reference substances. Further validation needs to be undertaken and appropriate reference substances (e.g. natural polymers as performance benchmarks) are required if such tests are to have 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”* but more detailed recommendations on preparation methods and assessment of influence of particle size after homegenisation is required.

In recent years several specific standard protocols have been adapted or developed for (bio)degradability testing of plastic materials (see also report of WP4). 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). These 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), to calculate the mineralization rate considering specific surface area is given in ISO 5148 (ISO, 2021a).
- Biodegradability of plastic materials in an **aqueous medium** is given in ISO 14851 and 14852 (ISO, 2018b, 2019a).
- Biodegradability of plastic materials in **soil** is given in ISO 17566 (ISO, 2019b), 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.
- 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, 2019c). Additionally ISO 22403 (ISO, 2020b) specifies test methods and evaluation criteria, ISO 23832 (ISO, 2021c) determines the degradation rate (thickness, mass, tensile

strength) and the disintegration degree, and ISO 22766 (ISO, 2020c) gives information for testing under real field conditions.

These test guidelines are usually following the degradation via indirect parameters such as O₂ consumption or CO₂ evolution, i.e. 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.

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

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 have been developed to assess effect of weathering (ISO and ASTM). 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/m²). 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. This changes during photoageing can be followed by determining changes in colour (ISO 4582; ISO (2017)) or also other methods for appearance, mechanical or other properties. For example, tensile properties can be determined using ISO 527. 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)).

Finally, in a limited number of standards weathering and (bio)degradation will be combined. For example 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 15–25 ± 2 °C (Meereboer et al., 2020). But usually, the standards recommend to measure biodegradation, physical degradation and/or mass loss in absence of sunlight.

3.3 Degradation data

Several compilations of available degradation data for polymers 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)), and Polman et al. (2020) covering natural biopolymers 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); Meereboer et al. (2020) etc.). Further relevant literature 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) and Open-Bio (2016). 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).

However, data on simulation studies according to OECD 307, 308 or 309 are not publicly available for polymers or at least rare. Studies using pure ready biodegradable test systems according to OECD 301

are rare as well. However, the available data indicate that synthetic polymers can be readily biodegradable, whilst in some cases natural polymer materials are not. 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 test system. For synthetic polymers data are usually available rather for biodegradable polymers than for clearly expected non-biodegradable polymers. Especially for (very) stable polymers, biodegradation data are rare. Often only non-guideline studies to consider effect of weathering and disintegration are available.

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 CO₂ 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.

3.4 Influencing parameters

Based on the information given above, it is obvious that some polymeric substances biodegrade in a different and more complex degradation process than (low molecular weight) soluble chemicals. In the case of polymers, it is due to their physical form and/or very large molecular size which prevents microorganisms from accessing large parts of the material. This may result also in different influencing parameters.

Usually, degradation (rate) of a (single) substance in the environment is not a substance inherent property but depends on the environmental conditions. The rate is influenced by the type of compartment and the concentration of suitable microorganisms in this compartment. In addition, temperature, oxygen content and pH will have significant impact on the result. For this reason, the result can vary considerably for different water or soil types. All these parameters will influence the degradation of polymeric material as well. For example, Pischedda et al. (2019) investigated the effect of temperature on the biodegradation of a commercial biodegradable plastic material in soil. Thereby the authors stated that the mineralization is *“perfectly described by an exponential model that was in agreement with the Arrhenius equation”*.

In contrast, the distribution of solid polymeric substances will be different to (single) soluble substances. The density may be a trigger value if for example the substance will be transported to the deep sea or will be present at water surface. In this context the wettability and crystallinity as well as the natural cover by biofilm will influence the density of the particles, and thus the settling potential.

Generally, biodegradation rates decrease with increasing molecular weight (MW), so that low MW constituents of a polymer are degraded more easily than higher MW material (Duis et al., 2021). This is especially true for water soluble polymers where this effect has been shown for PEGs with different molecular weight ranges (Bernhard et al., 2008; Duis et al., 2021; Eubeler, 2010; Eubeler et al., 2010). In this context it is important to repeat that even one group of substance could be divided in several sub-groups with significant different properties. For this reason, there is potentially high diversity even within one polymeric material.

The nano- and micro-scale structure such as degree of crystallinity influences biodegradation of non-soluble polymeric substances as well (Meereboer et al., 2020; Su et al., 2019). Amorphous or less-ordered regions degrade more easily than crystalline regions (Brueckner et al., 2008; Meereboer et al., 2020; Su et al., 2019). In general, the shape of a material plays an important role as a larger surface

area will promote degradation (Andrady, 1994; Haider et al., 2019). Urea formaldehyde resins with a lower F/U molar ratio, which showed crystalline regions, tend to be more resistant to hydrolysis than those with a high F/U ratio, which showed amorphous structure (Park and Jeong, 2011). This is linked with the degree of branching and the number of exposed methylol groups available to undergo the hydrolysis reaction. In conclusion, the crystallinity, morphology, shape and size are important influencing parameters for degradation rate.

The degradation rate of polymers is also influenced if the degradation is by surface or bulk erosion. Surface-mediated biodegradation may be driven by the ratio between surface and volume (ECETOC, 2020). For polymeric materials usually fragmentation by bulk erosion takes place, which may consequently result in an increased surface area. The increased surface area is then expected to result in faster degradation if the polymer is susceptible for biodegradation to occur (ECHA, 2020). As such powder form has the largest surface area to volume ratio and should have the fastest biodegradation (Meereboer et al., 2020). The influence of surface area on the biodegradation rate has been demonstrated for biodegradable plastic films compared to powder form of PCL, PBSA, PLLA, PBS and PHB (ECHA, 2020). However, the comparison between PHB films to PHB powder have shown that certain film thickness can show a comparable biodegradation rate (Meereboer et al., 2020). Chinaglia et al. (2018) and Tosin et al. (2019) evaluated the impact of particle size on biodegradability in soil of polybutylene sebacate (milled pellets), whilst and of a commercial biodegradable plastic material respectively. A relationship between the biodegradation rate and the available surface area was observed, and the specific mineralization rate (in mg/day/cm²) of the material tested determined. Both papers concluded that if it is technically feasible to test the polymer in a nanopolymeric form it could very likely satisfy the Organization for Economic Co-operation and Development (OECD) criteria of “ready biodegradability” for chemicals.

Overall, bioavailability is an important factor for polymer biodegradation, and thus structural as well as morphological characteristics will have an impact on the degradation rate. Polymeric structure, cross-linking, crystallinity, wettability, surface area and size are the main influencing factors. The weighting of these factors may be different between different types of polymers (solid, liquid, semi liquid, resins, water soluble or non soluble polymers). When comparing biodegradation studies and assessing persistence of polymers it is important to consider these factors in a weight of evidence approach.

3.5 Natural polymers vs Synthetic polymers

As stated previously polymers exist in nature as well. These so called natural polymers include natural rubber, cellulose, hemicellulose, starch, lignin, chitin, cutin. In fact, even DNA or proteins are strictly speaking polymers albeit not according to the definition of polymers under REACH, as they are not distributions but very precise macromolecules. Sometimes natural polymers will be 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 α -glycosidic bonds or stronger β -glycosidic linkages. Natural rubber or Latex is the polymer cis-1,4-polyisoprene.

Both natural and synthetic polymers, are formed by polymerization of many 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 as well as 2D and 3D structure (linear, branched, crosslinked, and networked polymers). These properties in turn will result in different (bio)degradation kinetics, e.g. some natural polymers are hydrolytically more stable than others.

Detailed evaluation of available information about similarities and differences between degradation potential of natural and synthetic polymers are given in a separate report (WP4).

Natural polymers are usually regarded as not a concern under real environmental conditions. For example, natural polymers are excluded from the restriction proposal for intentionally added microplastic (ECHA, 2020). 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 mass balance 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. The timeframe of the presence in different compartments could be highly variable depending on the type of polymer and the conditions.

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 reduced 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 which indicate that in some cases the natural polymer would meet the persistence criteria. For example, 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 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 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.

Overall, the results of these standard screening tests indicate that not all natural materials can be regarded as being rapidly biodegradable, and thus as being “non-persistent”. Indeed, the ability of current simulation tests to come to a final conclusion on persistency is missing for such materials. However, there is no doubt that many natural polymeric materials will fail the persistence trigger values given in Annex XIII (EC, 2011), as it is the intention of nature to form resilient materials for example for protection or skeleton constructions of organisms. Additional properties such as (bio)accessibility or bioavailability, the emission pattern and a host of real life factors which are not currently included in such studies (e.g. light, temperature extremes, physical damage, ingestion, inadvertent exclusion of competent fungal organisms etc.) plays a major role in making these natural polymers not a concern for the environment.

The conclusion which can be drawn is that, under the context of REACH Annex XIII many natural polymers would be determined to be P/vP. However, it is unlikely that they having a concern for the environment. This also needs to be recognized when assessing synthetic polymers, many of which would fulfil the P/vP criteria. For such polymers it would also be important to establish further properties to enable adequate hazard assessment.

4 Persistence assessment of Polymers

Many polymers are present on the market as polymer products, which include multiple constituents such as polymeric macromolecules of different molecular weights, residual monomers, residual starters, intentionally added substances (IAS) and non-intentionally added substances (NIAS) (ECETOC, 2020). Consequently, some of these constituents will not be regarded as part of the “substance” according to the polymer definition under REACH regulation (ECHA, 2012). However, the situation is more complex because stabilisers are considered part of the polymer substance. Thus for the persistence assessment it is actually necessary to consider the degradation of the polymer with its associated stabiliser.

It is intuitively obvious that polymers as a complex mixture will not result in one degradation rate for all components. However, fraction profiling may be possible resulting in a grouping of constituents with similar properties, especially with regard to expected degradation rates. Furthermore, the presence of stabilisers could be challenging, as it is intentionally added to the material to ‘stabilise’ the product and ensure slower degradation especially by UV radiation. In this case the leaching or degradation of the stabiliser in the material will also influence the degradation of the polymer product.

As a consequence, the exact composition of the polymer substance, more precisely the polymer product, may influence the applicability of a specific (bio)degradation test method, and the interpretation of the results. The identity and composition of the polymer over time in the environment (i.e. as leaching of the stabiliser occurs) is thus of interest to decide on valuable information for (bio)degradation, and should in a first step be evaluated as accurate as possible.

Another specific issue is the presence of polymer substances often as solid and non-water soluble particles. Some polymer products are of high molecular weight and exhibit limited solubility (ECETOC, 2020). The existing persistence assessment test methods, mostly developed for testing substances with high physical and biological availability, may not be well suited for (practically) insoluble polymers, and merit further development work for adapting those to polymers (Epoxy Europe, 2021). It is also important to assess how polymers may be degraded in the environment and assess how this can be incorporated/factored into persistence assessments. For example, polymer particles may be degraded by surface erosion or bulk erosion (Albright and Chai, 2021; Meereboer et al., 2020; Su et al., 2019). During surface erosion the size of the particles will change but not the number of the particles. In contrast during bulk erosion the number of particles will change but not the total mass of the particles. Both will result in a loss of polymeric material in the environment, which can be considered as true (bio)degradation in the sense of persistence assessment if we can bring evidence that the loss of material is mineralized or at least incorporated into biomass. However, different analytical techniques are necessary to differentiate between both these degradation processes (Albright and Chai, 2021). Another possibility is the fragmentation, whereby the number of particles and the mass per particle will change. However, in this case no mass loss can be observed. This raises the question as to whether this process could be considered to be analogous to the formation of transformation products if the resulting fragments produced are significantly different to the starting material.

Specific issues will also be encountered during evaluation of certain polymer groups which have been previously identified in section 2.3. For example, the pilot project of the EPDLA (European Polymer Dispersion and Latex Association) identified several issues for their polymers (EPDLA, 2021). An issue they encountered which has yet to be solved is: “How to perform studies on polymers for registration purposes if the isolation of a polymer is not possible without destroying its physico-chemical structure (e.g., polymer dispersions are manufactured in the presence of emulsifiers and other additives which cannot be removed from the dispersion).” In addition, the requirement of alternative methods for determining the number average molecular weight (M_n) has been highlighted, especially for certain

polymers which are partially insoluble or where cross-linking occurs during Gel permeation chromatography (GPC) analysis. One such alternative method could be the use of e.g. the OH number for polyols and other proxies for other types of polymer chemistry where GPC is technically not meaningful.

Four major challenges have been identified for assessing polymer biodegradation by Albright and Chai (2021): (1) a lack of standardization in polymer biodegradation testing, (2) the long durations required in biodegradation testing, (3) demanding analytical methods, and (4) a lack of a framework for assessing the overall persistence of polymers. However, it is the last point and the need to develop a conceptual framework for polymer persistence assessment that this report has focused on.

4.1 Procedure of Standard Persistence assessment within PBT assessment, and applicability to Polymers

Criteria for the identification of persistent, bioaccumulative and toxic substances (PBT substances), and very persistent and very bioaccumulative substances (vPvB substances) as well as the information that must be considered for the purpose of assessing the P, B, and T properties of a substance are laid down in the Annex XIII of REACH regulation (EC, 2011). According to this Annex, the persistence assessment is usually based on the evaluation of simulation tests. These could be (a) Results from simulation testing on degradation in surface water; (b) Results from simulation testing on degradation in soil; and (c) Results from simulation testing on degradation in sediment. In addition, other information such as information from field studies or monitoring studies can be used, if they are suitable and reliable. However, if simulation tests are not available – for whatever reason – in a first step information shall be considered relevant for screening on persistence.

The integrated testing strategy (ITS) of REACH guidance R.11: PBT/vPvB assessment (ECHA, 2017b) starts with the screening. This includes first the evaluation of the evidence for readily biodegradable (including modified test systems), followed by other screening information such as enhanced screening tests or inherent biodegradation test data, and the consideration of further information useful for a Weight-of-Evidence approach.

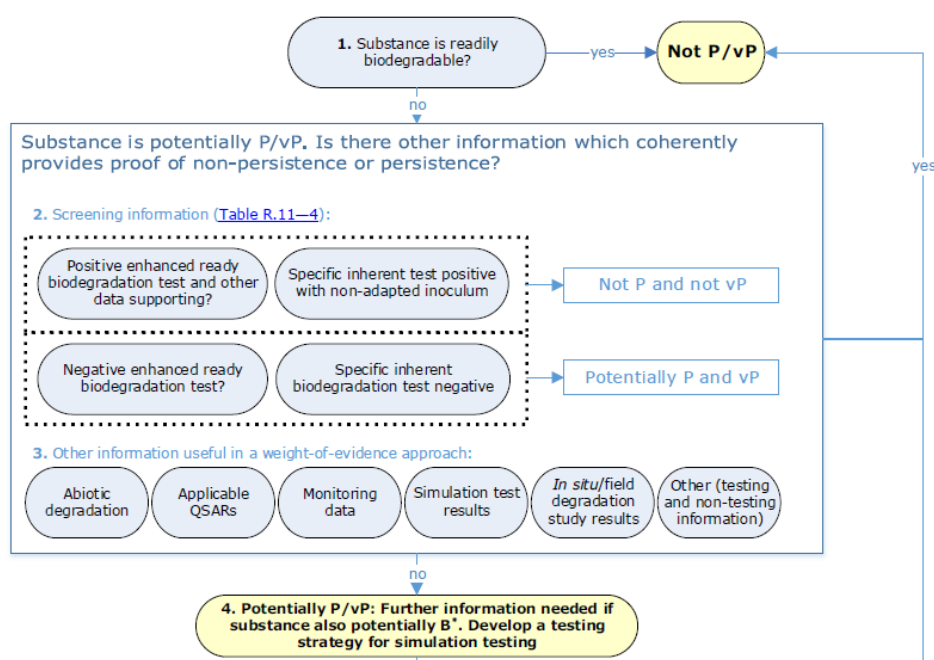


Figure 2: Integrated Assessment and Testing Strategy (ITS) for persistence assessment within PBT/vPvB assessment according to ECHA (2017b): Figure R.11-3 (upper part)

Please note, a negative result in a screening test will only result in ‘potentially P/vP’, i.e. does not necessarily mean that the substance will persist in the environment and will not be degraded under relevant environmental conditions. A negative screening only indicates that additional information is necessary to give evidence to exclude persistence. For this reason simulation testing have more weight in assessing persistence according to the Annex XIII (EC, 2011).

If the substance is based on the screening potentially P/vP, further information or testing is required. In this case usually degradation in surface water will be tested first, or other compartments if necessary, i.e. if simulation testing in surface water is technically not feasible or if there is another compartment of specific concern (see Figure 3). A justification has to be provided if any environmental compartment other than surface water is chosen for the initial simulation degradation testing. If the substance or its degradation products are concluded to be persistent or very persistent, there is no need for further testing for persistence assessment. This is followed by a discussion of the concern for the remaining compartments, i.e. whether the available information is adequate to conclude on persistence assessment for all or some of the remaining environmental compartments for which there are no testing data. If the available data are not sufficient for drawing conclusions in (an)other compartment(s), further data generation is necessary.

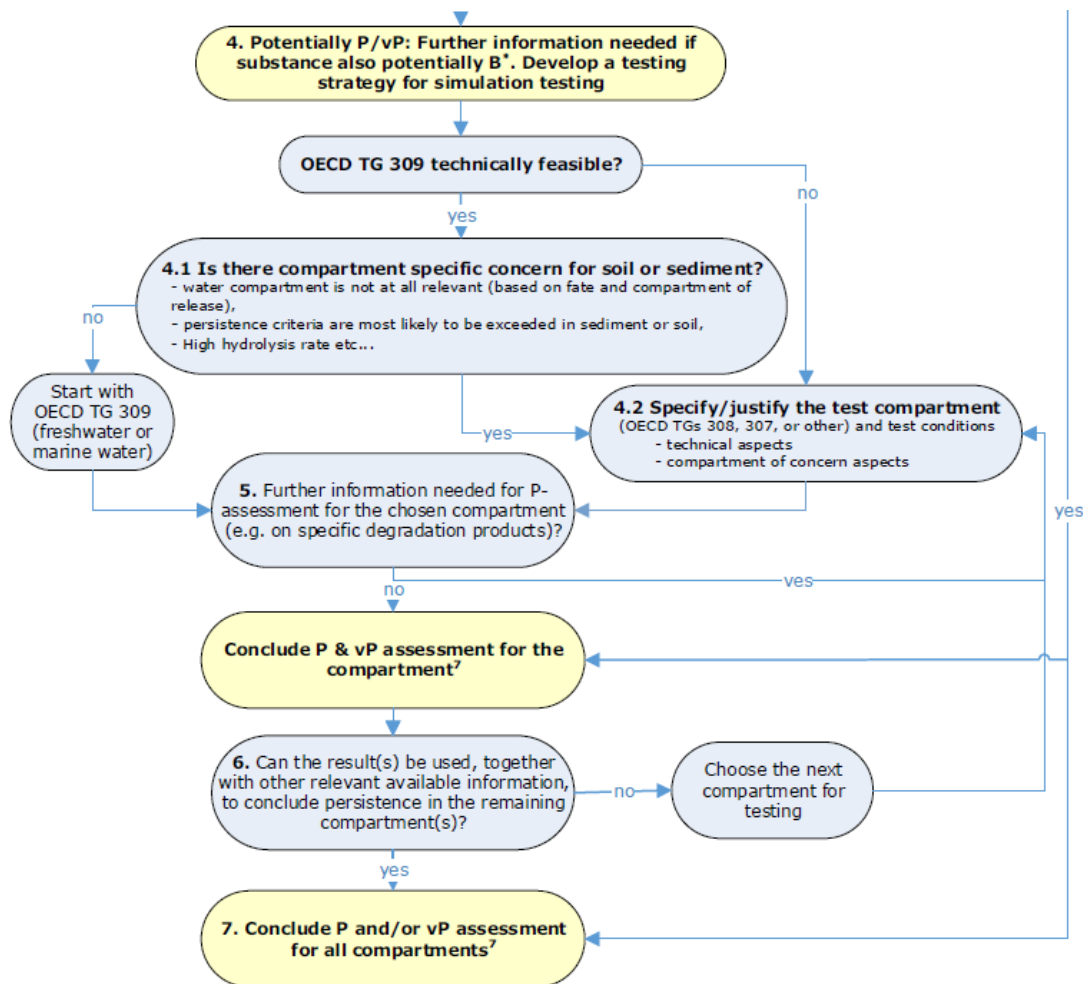


Figure 3: Integrated Assessment and Testing Strategy (ITS) for persistence assessment within PBT/vPvB assessment according to ECHA (2017b): Figure R.11-3 (lower part)

4.1.1 Screening tests

Biodegradation screening tests are designed to evaluate the intrinsic biodegradability of substances. Thereby the biodegradability is generally determined using diluted inocula (derived from a variety of sources: activated sludge; sewage effluents (unchlorinated); surface waters and soils; or from a mixture of these), and a non-specific parameter such as oxygen consumption, CO₂ evolution or dissolved organic carbon (DOC) removal. These values will be compared to information about the starting DOC, the theoretical oxygen demand (ThOD) or the theoretical CO₂ evolution (ThCO₂), so that the screening test systems are providing usually the magnitude of mineralization. Pass level criteria for screening test are 60% or 70% mineralization within a specific time. In the screening test systems relatively high concentration are needed to be above the background levels of the systems (blanks). These concentrations are reflecting a worst-case situation of the ratio substance / inoculum, and thus are usually not environmentally relevant.

Generally, screening test systems can be divided in ready, modified, enhanced and inherent biodegradability test systems.

Ready biodegradability test systems

The most stringent screening test are the ready biodegradability test systems (OECD TG 301 or 310). Ready biodegradability tests must be designed so that positive results are unequivocal. Given a positive result in a test of ready biodegradability, it may be assumed that the substance will undergo rapid and ultimate biodegradation under most environmental conditions (ECHA, 2017a).

Although developed to determine the biodegradation potential of single substances consisting of small and water soluble molecules, the ready biodegradability test systems are in principle applicable to the evaluation of polymers, as only information is needed on O₂ consumption or CO₂ evolution during the degradation processes. However, since polymers can be complex mixtures, it can be difficult to adequately quantify the ThOD or ThCO₂ (ECETOC, 2020). Elemental analysis and/or total organic carbon analyser can be appropriate in some cases. Alternatively the chemical oxygen demand (COD) of the mixture can be measured and used for comparison with the O₂ consumption, but if it not represent the complete oxygen demand for mineralization this approach will overestimate the biodegradability. Methods relying on the measurement of DOC may not be relevant for poorly soluble or non-soluble polymers (ECETOC, 2020).

For ready biodegradable test systems an additional criterion is used: substances will commonly be regarded as ready biodegradable only if the 10 day window criterion is met, i.e. the pass level of ready biodegradability is reached within 10 days after start of biodegradation (start means exceeds the 10% level). However, polymers often undergo sequential biodegradation of the individual structures. In this case it does not make sense to apply the 10 day window criterion (OECD, 2006). Further, the pass level criterion implies total degradation by considering that mineralization is often not complete, thus assumes that 30-40% of the organic carbon of the test substance is either assimilated by the microbial biomass for growth or present as products of biosynthesis (ECHA, 2017a). However, for polymers (and UVCB) this situation is more complicated. Even if mineralization greater 60% or 70% is observed it is still questionable if all constituents are biodegradable, or some are not-biodegradable. For example PEGs with different molecular weight have different kinetics (Eubeler, 2010). If a mixture of PEGs will be investigated, the total mineralization could be > 60% but based only on the degradation of the low molecular weight compounds. An additional example is a polymer of two different monomer where one is biodegradable and the other not. In this case, the total mineralization could be again > 60% depending on the ratio of both monomers, but the substance result in a persistent transformation product. For this reason a high degradation will eventually not indicate complete mineralization of all material. On the other hand, the material (all individual constituents) is often similar, so that a high

degradation observed can indicate the potential of complete mineralization of all constituents. As a consequence for each polymer justification is necessary to provide evidence to explain and substantiate that results from screening tests are reliable. Assuming it is technically feasible, there is also the option to include specific analysis of the contents of the test flasks at the end of the test to demonstrate what types of molecules remain in the test vessels. An additional consideration is that the applicability of pass/fail criteria for the OECD TG 301 and 310 studies is not demonstrated for polymers (ECETOC, 2020).

Another important issue of polymers with the ready biodegradability test systems is the limited bioavailability if the standard conditions will be used. For example the very high concentration usually used result probably in lots of undissolved test substance in the test system, and in mass transfer issues for polymers with low water solubility. This is an issue not alone for polymers but for all substances with low water solubility and is already mentioned in the R.7b guidance, resulting in the recommendation of modified ready biodegradation test systems (ECHA, 2017a), which are regarded as true Ready Biodegradability Tests. For example carriers such as silica gel are proposed to increase bioavailability. This approach is generally accepted for single substances. However, carriers are usually not applicable for solid but only for oily/viscous substances. For this reason, carriers are of limited use for solid polymers. An alternative to overcome the limited bioavailability is an extension of test duration (ECETOC, 2020). An extension of test duration is in the standard approach considered in the enhanced biodegradation screening tests (see below).

Nevertheless, further adaptation or specification might be necessary to measure solid materials, as Ready Biodegradability Test systems have been developed for solutions or suspension only. Under the strict conditions of these test systems, solid materials are difficult to be tested and the results should be carefully interpreted. Surface-mediated biodegradation of particles may be driven by the ratio between surface and volume. Acceptable adaptations such as previously mentioned attempts to prepared standardised particle size of the test substance after homogenisation of solids should be defined.

In conclusion, Ready Biodegradability Test systems should in principle be applicable for water soluble polymers. However, definition of water solubility of substances and especially of polymers or surfactants is another issue, not discussed here. Water solubility will influence the bioavailability, and the limitation of bioavailability could have an influence on the mineralization rate, so that a prolongation of test duration becomes necessary, for example up to 60 days (see enhanced biodegradability test systems or ISO test systems). Some information about results for polymer material in Ready biodegradability Test systems is available in the literature. For example McDonough et al. (2017) tested several microparticles in the OECD TG 301B. Some of the tested material can be regarded as readily biodegradable, but some (also natural polymer material) still not pass the criteria. It is expected that most type of polymers will not meet the criteria.

However, to reiterate a negative result in a test for ready biodegradability does not necessarily mean that the substance will persist in the environment and will not be degraded under relevant environmental conditions. A ready biodegradability test is only a screening test, and if that test could not demonstrate that the substance is readily biodegradable then further testing under less stringent test conditions should be considered at the next level (ECHA, 2017a).

Enhanced and inherent biodegradability test systems

According to REACH guidance R.7b (ECHA, 2017a), *“if a substance does fail to reach the pass level for the ready biodegradability, results from other screening tests (enhanced ready tests or tests on inherent biodegradation) may be useful additional testing to show that a substance is not persistent. [...] A number of potential enhancements to the ready biodegradation test have been identified. These*

enhancements have been proposed for the determination of persistence in vPvB/PBT assessment only but are not to be used for Classification and Labelling and quantitative exposure and risk assessment. These enhancements are designed to help to improve the environmental relevance of biodegradability assessments for persistence assessment only without the immediate requirement for simulation level testing”.

Enhanced biodegradation screening test systems could include according to REACH guidance R.7b (ECHA, 2017a) prolongation of test duration and/or testing in larger vessels. *“The purpose of those enhancements should only be to compensate the poor bioavailability to the degrading microorganisms of poorly soluble and/or adsorptive substances, but should not be used to induce additional adaptation of the inoculum”* (ECHA, 2017a). For most of the polymers, which are often poorly water soluble substances, the bioavailability indeed limit the mass transfer and thus degradation rate. The prolongation of the test duration is in these cases a precondition to observe ultimately the final degree of total biodegradation (plateau). However, the test must in any case be terminated within 60 days (ECHA, 2017a). In addition, conducting biodegradation tests using larger volumes of environmental waters increases the probability of introducing sufficient number of competent microorganism into the test vessel (ECHA, 2017a).

Both enhancements are generally possible for polymers, and it is expected that it will increase the likeliness of a positive test result and could provide additional information on potential environmental persistence (i.e. if biodegradation does not meet the pass criteria but is continuing but simply slow due to the restrictions of bioavailability or if a plateau is reached). For example Eubeler (2010) has shown that prolongation will result in sufficient biodegradation of PEGs with higher molecular weight. However, justification should be given considering specifications given in R.7b and R.11 (ECHA, 2017a, b) for interpretation of enhanced biodegradation screening test results. The same pass criteria set for ready biodegradability tests should be applied without the 10-day window. However, many polymers will fail these ready tests and an additional level of assessment appropriate for these difficult to test substances is required.

The next step would be to consider OECD 302 test series as these have been developed to determine the inherent biodegradability of organic substances, and may be used directly for the assessment of environmental persistence of substances. These test systems *“allow prolonged exposure of the test substance to microorganisms and a low ratio of test substance to biomass, which offers a better chance to obtain a positive result compared to tests for ready biodegradability”* (OECD, 2006). According to ECHA’s ITS, results of a Zahn-Wellens test (OECD TG 302B) or MITI II test (OECD TG 302C) only (not SCAS-test) may be used to confirm that the substance does not fulfil the criteria for P provided that certain additional conditions are fulfilled (ECHA, 2017b).

For polymers, similar limitations as described for ready biodegradability test systems apply for both enhanced and inherent biodegradability test systems. For example, these test systems are in principle applicable to the evaluation of polymers, but this will be complicated by having adequate ThOD or ThCO₂, and that evidence is needed that the results produced are reliable and reflect the biodegradability of all constituents.

Other useful information under ITS of REACH for persistence assessment according to ECHA (2017b)

In this part of the ITS, any other relevant information should be gathered in a Weight-of-Evidence approach. This include QSAR, anaerobic degradation, any other degradation studies, abiotic degradation (hydrolysis, photodegradation), field studies, monitoring etc. Thereby, QSAR are often an important tools, as they allow to generate biodegradation or partitioning data for a large number of (theoretical) constituents. However, most QSAR are usually out of domain for polymeric substances.

The available Marine biodegradability screening tests (OECD TG 306, Marine CO₂ Evolution test, Marine BODIS test, and the Marine CO₂ Headspace test) are variations of the ready biodegradability test systems. However, since these studies use environmental samples as inoculum, they tend to demonstrate great variability (ECETOC, 2020). For polymers, similar limitations are present as described for ready biodegradability test systems. The enhancements mentioned above may also be applied to standardised marine biodegradability tests (ECHA, 2017b). Furthermore, if marine biodegradation studies are undertaken it is important that the limitations of these tests and recommendations to improve their reliability as proposed by Ott et al. (2019) and Ott et al. (2020) are considered even if not polymer specific.

Similar screening test systems are also available for assessing degradation in soil (OECD TG 304A Inherent in soil) and in sediment (Junker et al., 2019). However, these methods are currently not specifically mentioned in the P assessment scheme under REACH, but are supposed to be covered within this “other” section.

There are also plastic weathering guidelines which will be discussed later in section 4.2. As explained above abiotic degradation (hydrolysis and photodegradation) plays a major role in the weathering of polymers/plastics and their degradation. For this reason, standardized evaluation of abiotic degradation could give relevant information for the Weight-of-Evidence approach. The hydrolysis test (OECD 111) is often not useful for substances with low water solubility. However, *“the test may still be important in certain circumstances, for example where hydrolysis occurs at the surface of particles of the undissolved substance leading to more soluble products, but may be considered on a case-by-case basis if needed for risk assessment purposes”* (ECHA, 2017a). Several (OECD) guidelines exist to evaluate photodegradation but as stated previously this removal method is not given due consideration by ECHA in persistence assessments. The justification being due to the large variation in the light available in different environmental compartments (ECHA, 2017b). Furthermore, for polymers the analytical verification required to support these tests is complicated by the complex nature of the substances. Moreover identification and quantification of transformation products will often also be difficult due to missing adequate analytical methods. Overall, the consideration of abiotic degradation within the persistence assessment will be a case-by-case discussion of the extrapolation to real environmental conditions and the universal validity. For example, the degradation half-lives obtained in a hydrolysis test cannot be compared to the persistence criteria of Annex XIII (ECHA, 2017b). There also may be scope to consider photodegradation for certain polymers in water if their properties indicate these will float and therefore remain at the air/water interface.

4.1.2 Simulation tests

Simulation tests aim at assessing the rate and extent of biodegradation in a laboratory system designed to represent either the aerobic treatment stage of sewage treatment plant (STP) or environmental compartments, such as fresh or marine surface water or sediments, or soil (OECD, 2006). These studies are considered to be more environmentally realistic than the screening studies. Low concentration of test substance is typically used in tests designed to determine the biodegradation rate constant, whereas higher concentrations are normally used for identification and quantification of major transformation products for analytical reasons.

Simulation biodegradation test methods relevant for P assessment include OECD TG 307, 308, and 309. Under current ECHA guidance simulation testing for sewage treatment plant (STP, 303A-B and 314A-E) cannot be used on their own within persistence assessment. However, these could probably be used as a part of the weight-of-evidence approach or for justification of the remaining concern. For example, Fenner et al. (2020) published an approach for read-across from sludge to soil. In general, it is

recommended to start testing with the OECD TG 309 if it is technically feasible. However, if there is evidence that the OECD TG 309 does not provide means to reflect the persistence of the substance in the environment, other environmental compartments may be considered as first test environment (ECHA, 2017b).

From the simulation test, information will be obtained on mineralisation, primary degradation and the type and amount of relevant metabolites. For comparison with the criteria (section 1.1.1 of Annex XIII), half-lives have to be derived from these simulation testing. These half-lives are strictly speaking only valid for first order kinetics. If other kinetics (e.g. biphasic) have been obtained, alternatively the disappearance time for 50% degradation can potentially be used, or the slowest half-live of the biphasic kinetic. Half-lives can also be estimated based on the DegT90 values (DegT90/3.32) according to the FOCUS guidance (FOCUS, 2014). The latter is not described in the REACH guidance R.11 (ECHA, 2017b).

In addition, as already mentioned above, *“where only primary degradation is observed, it is necessary to identify the degradation products and to assess whether they possess PBT/vPvB properties”* (ECHA, 2017b). For this reason, besides B and T assessment information from biodegradation screening and/or simulation testing is necessary for every relevant metabolite as well, to compare the results with the persistence criteria. Usually radiolabelled substance is necessary in the simulation tests to trace the primary degradation of the parent substance and all the transformation products. If degradation is observed, it is sometimes difficult to identify all the transformation products, and their degradation half-lives.

For polymers, the requirements described above present several challenges to the feasibility and ability to perform acceptable simulation studies. This has been recognised by ECHA and RAC who recently highlighted the practicality and applicability of simulation test methods to microplastic test materials (ECHA, 2020). For polymers, the application rates of test substance to the compartment and radiolabelling may be particularly challenging, the application rates and the limit of quantification of an appropriate analytical methods have to be aligned, mass balance and identifying and quantifying the spectrum of metabolites (by-products of biodegradation). The latter is challenging even with a radiolabelled backbone. Depending on the complexity of the polymer, radiolabelling to clarify degradation pathways for all potential side chains may be even impossible. Furthermore, simulation tests have shown limited applicability to non-polymeric UVCBs, and similar limitations have already been observed for complex polymer products with very dissimilar components (ECETOC, 2020). This list can be supplemented by difficulties to have an appropriate analytical method for the whole complex substance and to realise a sufficient recovery, or rather to decide on an appropriate endpoint of the analytical method to follow the degradation.

Polymers are macromolecules consisting of repeating monomer units. Sequential degradation is expected, but also fragmentation is possible by attack at structural breaking points, followed again by sequential degradation of the fragments. As a result a high number of (relevant) transformation products will be expected, and following the current ECHA guidance these transformation products may need to be evaluated for their persistence potential in order to conclude on the persistence for the parent polymer. This would result in a high number of additional simulation tests required with the same challenges and analytical issues. In addition, it is highly likely that not all transformation products could be identified or isolated so that individual testing is not always possible. An agreed explanatory guidance may be advisable to decrease the effort to the most critical transformation products.

For this reason it becomes necessary in an adapted persistence assessment framework for polymers to decide first on the relevance of the different transformation products. Moreover summing up the

degradation time of a high number of transformation products, with each are having a primary degradation time below the persistence criteria, may result at the end in a very long total degradation time, and thus still in long presence of the polymeric mass in the environment.

Finally, it should be highlighted that according to Annex XIII the requirement is to draw a conclusion for all three (five) environmental compartments. In general, results of a single simulation degradation study cannot be directly extrapolated to other environmental compartments (ECHA, 2017b). However, in the evaluation of remaining concern, it is possible within a Weight-of-Evidence approach to justify that the results are sufficient to conclude on (non-)persistence in other compartments, i.e. if read across (qualitative or quantitative if reliable) is possible from one simulation test to the other compartment. But again, an agreed explanatory guidance may be advisable to illustrate the situation where it is possible and decrease the effort to the most critical compartments. For polymers, it has to be clarified under which conditions approaches such as multi-media modelling or adaptation of these approaches can be used to evaluate the remaining concern.

4.2 Alternative test systems and approaches

To deal with the challenges specific test systems as well as methodologies for testing strategy and persistence assessment have been developed for polymers.

4.2.1 Specific test systems developed for polymers

As described in section 3, 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.

These test guidelines are usually following the degradation via indirect parameters such as O₂ consumption or CO₂ evolution, i.e. mineralization. By doing so they will overcome the analytical challenges of the simulation testing, but the same limitations as for the ready biodegradability test systems as well as the enhanced or inherent test systems exist. In addition, these incubation systems with respirometric measurements will not allow for the closure of mass balances on the polymer carbon added to the test system, and they offer no information on the incorporation of polymer-derived carbon into soil microbial biomass (Sander, 2019). These limitations can be overcome by using carbon isotope-labeled instead of unlabeled polymers, whereby the use of ¹⁴C-labeled polymers is often impractical due to regulations and safety measures. Instead, the use of stable ¹³C-labeled polymers is more viable (Sander, 2019).

The ISO guidelines for aqueous medium use diluted sewage sludge as inoculum, and may be pre-conditioned but normally not pre-exposed, and are thus generally comparable to the OECD screening test systems. For the marine test systems natural environmental samples are used in agreement to the OECD TG 306 although more recently it has been recognised that pre-concentrating naturally occurring microorganisms from seawater using techniques such as tangential flow filtration can improve the reliability of marine biodegradation tests (Ott et al., 2019; Ott et al., 2020). For soil (ISO 17566), addition of matured compost is recommended (40 g/kg) in order to stabilize the microbial activity. The available test results indicate that soil tests without mature compost have potentially lower percentage biodegradability for the reference substance in comparison to test which applied matured compost. For example, in the experiments published by Gómez and Michel (2013) the reference cellulose paper did not reach 60% or 90% after 6 months and 2 years, respectively. On the other hand

the increased respiration due to the compost will eventually result in the need of much more test material to be significant different to the blank (200 mg test material with 200 g soil is recommended). Additionally comparable to the OECD screening test, the ISO test systems will be performed at 20-25 °C (the soil test up to 28 °C).

In contrast, the tests used to assess polymers are conducted over a much longer test duration in comparison to the OECD test guidelines (aqueous medium 2 month (60 days), soil 6 month (and up to 2 years)). Furthermore, specific information are given on the application of the solid test material. For example, according to ISO (2019a, 2019b), the test material should preferably be used in powder form, but it may also be introduced in the form of films, pieces, fragments or shaped articles; a particle-size distribution with its maximum at 250 µm diameter is recommended. Further information is also given in a separate guideline for methods for the preparation of samples for biodegradation testing of plastic materials (ISO, 2012).

Regarding the test results, these are expressed usually as the percentage degradation at the plateau similar to the OECD guidelines. However, ISO 17033 (study for the degradation of mulch films in soil) will give additionally the possibility to give the result as a benchmark to a reference compound such as cellulose. In this test the polymer substance should achieve > 90% degradation in both cases (i.e. relative to reference or absolute), and the pass level is thus higher in comparison to the pass levels of the OECD guideline, but is in agreement to the longer duration of up to 2 years (please note a DegT90 of 2 years is comparable to a half-life of 180 days). Using benchmarking by incorporating a well-known reference with similar properties like the test material is of interest and value as it helps solves a number of confounding factors related to interpreting the test data e.g. the issues on the results coming from different microbial activities, from different soil types or the addition of matured compost, as well as from the influence of the size of particles and the wettability. However, microbial degradation will always incorporate an amount of carbon into microbial biomass, which depends on the molecular structure (Trapp et al., 2018). For this reason, benchmarking is strictly speaking only reliable if particle size and molecular structure is similar. It is recognised that benchmarking places a different view on the result in comparison to those for the standard approach of screening tests, and consequently, the environmental relevance or relevance for P assessment of this benchmarking should be discussed. In the ECHA RAC opinion on the proposal for a restriction for intentionally added microplastics (ECHA, 2020), this (bio)degradation relative to a reference is generally applied to all ISO test guidelines (group 4, see Annex) although this benchmarking is explicitly mentioned only in some specific guidelines.

Overall, as degradation potential in specific compartments (surface water, marine water/sediment, soil) are measured in the polymer specific ISO (or ASTM) test guidelines, these test systems can be regarded as in-between the enhanced biodegradation test systems and the simulation testing, or the test guideline for aqueous medium even comparable to an enhanced biodegradation test system. However, they should still be regarded as screening test systems only. It is not appropriate to compare kinetics (DT50 or DT90 values) from these type of screening tests with the criteria of Annex XIII. Nevertheless the test duration are covering the time for vP from the Annex XIII criteria, so that positive test results of mineralization in ISO test systems indicate that removal rate in environment is expected to be in agreement with the requirements of P assessment. For this reason they will complement the other information on screening within the WoE approach. However, validation of positive ISO results with OECD simulation test results is advisable. This could be very difficult at the moment because simulation test data for polymers are rare or not available and expected to be extremely technically challenging. Another option would be if there are any monitoring data available, these can be used to substantiate that substances with a positive test results are degraded (removed) in the environment (i.e. monitoring of environmental fate of polymers discharged into the environment).

In addition, some ISO test systems have been developed to follow the degradation during composting of biodegradable plastic materials. Similar to the OECD testing guidelines for fate and behaviour in sewage treatment plants, these test systems are currently only considered by ECHA as supporting information with regard to the P assessment. However, the results could be used in a Weight-of-Evidence approach as supporting information.

Environmental **weathering**, e.g. by sunlight (UV) which promotes formation of C-O bonds, is often the initial process in degradation of many polymers. As mentioned above standard test systems (ISO, ASTM) are available to measure the effect of weathering under laboratory (or natural) conditions. These test systems measure the effect of irradiation on chemical ageing, but also on appearance, mechanical or other properties. They are usually undertaken to provide prediction of material durability, and typically not used for persistence assessment. Whereby for material durability the focus is more to get information on the minimum stability, in persistence assessment the conditions should be to get information on the maximum duration of stability in the environment. However, some information is still of value for persistence assessment, but it has to be justified in the weight-of-evidence approach if the conditions are representative for real use conditions and thus the results useful as supporting information. Please note again, that data derived from photodegradation cannot be used on their own within persistence assessment under the ECHA guidelines (ECHA, 2017b). Moreover, as already mentioned even an extensively weathered, embrittled plastic material is no guarantee of subsequent biodegradability of the meso- or microplastic fragments (Andrady, 2011). Nevertheless, these studies can at least provide important information on relevant fragments and/or transformation products. If exposure of the environment by the polymer is primarily due to disintegration and fragmentation, it seems sensible to evaluate if the particles produced during the fragmentation process give cause for concern due to their persistent and bioavailable properties. This can be realised by pre-treatment of the neat polymeric material before applying it in the biodegradability test and/or use tests that combine multiple processes. Another option is to perform the test separately, and identify in a first step the transformation products within the weathering test system, and in a second step evaluate the relevance of the identified transformation products by QSAR or experimental investigations. It can be seen that many of the polymers cannot follow standard chemical persistence assessment approaches and often needs a stepwise approach to include further processes. For example, in 2018 ASTM published a “Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation” (Meereboer et al., 2020). This guide provides a framework or road map to compare and rank the controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal and photooxidation processes as well as the biodegradation and ecological impacts in defined applications and disposal environments after degradation.

Non-guideline tests often assess the degradation only by measuring unspecific parameters or the loss of functionality and as such are not directly related to the microbial conversion of the carbon. These test parameters such as visual disappearance of plastic, plastic mass loss, a decrease in the tensile strength, shortening of the average polymer chain length, or microbial growth are often considered as ill-suited to assess plastic biodegradation (Zumstein et al., 2019). However, they indicate that material or substance properties have altered, and they could potentially be used depending on the specific results to get supporting information on degradation pathways and primary degradation, or potential fragments or even transformation products, and to decide on further testing strategy.

Some non-guideline studies provide promising approaches such as alternative endpoints. Measuring the conversion of the carbon into microbial biomass using carbon isotope-labeled plastics as shown in Zumstein et al. (2018) is a promising supporting information to the mineralization. Development of appropriate chemical extraction methods are an important tool to determine biodegradation of

polymeric substances under environmental conditions, as shown by Nelson et al. (2020). In addition, the biodegradation of solid, non-soluble polymeric substances may depend on the surface area, and may be driven by the ratio between surface and volume (ECETOC, 2020; ECHA, 2020). For this reason, to compare results from biodegradation studies, these should be normalized, or a default size of the material should be recommended for P assessment. However, this mechanism of degradation from the surface to the inside of the particle provides the potential to assess alternative endpoints such as the specific surface degradation rate (SSDR) as recommended by Chamas et al. (2020). Ultimately, the approach taken has to be evaluated case by case to ensure and justify that the information obtained can be put on a level with the half-lives from standard test systems.

Often several test systems may be required. For example, SAPEA (2020) recommends to use a combination of laboratory tests, mesocosm test and field test to evaluate the degradation of plastics. As mentioned above, an overview of available information from **field/mesocosm studies** is given in Burgstaller et al. (2018). These field/mesocosm test systems have the advantage that they better simulate real environmental situations, e.g. the effect of sun-light or tidal forces on plastic articles. On the other hand, it is not a closed system, so that any (very) mobile degradation product (CO₂, small molecular weight transformation products) cannot be followed. This reduces the potential endpoints of such test systems to visual inspection of the resulting article, investigation of the surface and the functionality, and measurement of the mass loss in this article. These test systems are beneficial for the evaluation of the serviceableness of the articles for their intended use, however extrapolation on degradation of the constituents, i.e. polymers, is difficult. The utility of such tests to provide data for persistence assessment of the polymers is limited and should be justified case-by-case.

4.2.2 Methodologies

Generally two tasks are necessary to select the most appropriate approach/strategy:

- a) Selecting the most appropriate method for polymer (bio)degradation testing
- b) Interpretation of the results for persistence assessment

When selecting the most appropriate method for polymer (bio)degradation testing, it is critical to address its methodological limitations for the assessment of the given polymer (ECETOC, 2020). However, some technical limitations may be addressed by appropriate adjustments of the method. For example, if poorly soluble and particulate polymers exhibit reduced bioavailability in specific test systems, either due to transfer limitations in dilute test systems and/or high sorptivity, this might be addressed by changing the test configuration and/or the dosing procedure, and/or by extending the duration of the test (ECETOC, 2020). Further, as mentioned above many polymers are present as polymer products that include multiple constituents, which might biodegrade at individual kinetics. Where feasible, the duration of a biodegradation test should generally be extended until complete mineralisation of both the polymeric substances and all of the further constituents can be observed (ECETOC, 2020).

In addition, monomers or low molecular weight (LMW) constituents may be available in the polymer mixture. These fractions with higher physical and biological availability are more easily applicable in the standard test systems, and may be considered as a key constituent. If the test demonstrates that the fractions are not degradable in sufficient time, i.e. the degradation will be higher than the criteria given in Annex XIII, then by default the complete polymer is regarded as persistent as it contains at least a persistent constituent or probably forms it as a transformation product. On the other hand, if these fractions are degradable, the formation rate of these (transformation) products have to be evaluated to decide on the overall degradation time of the whole substance.

In accordance with the standard approach it is also possible to test in a first step the compartment of specific concern, and afterwards evaluate the remaining concern on the untested compartments, i.e. give evidence whether the available information is adequate to conclude on persistence assessment. Thereby multimedia modelling might be a promising approach for single substances to justify on the significance and the impact of some compartments on the overall persistence. However, the standard multimedia modelling is not appropriate for all polymers especially if the polymer exist as particle. It might be appropriate if polymers are water-soluble. For particles other transport processes are relevant, so that “new” modelling approaches have to be developed. As soon as these are available, these might be used to give evidence to justify the compartment of specific concern.

Several different approaches have been described in the literature, and will be discussed in the following for the applicability to polymer persistence assessment.

Microplastic biodegradation assessment

Biodegradability testing of microplastic (MP) has been discussed during evaluation of the MP restriction proposal (ECHA, 2020). If MP is biodegradable their use will not be restricted. Criteria for demonstrating (bio)degradation of MP and ECHA RAC-52 scheme for biodegradability assessment of MP are given in the restriction report. In the following only some results are highlighted and discussed.

In total, the Rapporteurs together with an ad-hoc RAC working group developed a series of eight scenarios comprising different approaches to the tests considered necessary to justify a derogation from the proposed restriction (including the Dossier Submitter’s (ECHA) proposal and the RAC scheme discussed at RAC-52) and systematically evaluated each of them in detail. The eight scenarios were developed based on either comments received in the consultation or in response to uncertainties identified in the Dossier Submitter’s proposal.

RAC (ECHA, 2020) considered that *“the criteria for derogating biodegradable polymers should be more stringent than proposed by the Dossier Submitter. Specifically, ECHA RAC considered that where the results of tests from groups 4 and 5 were used to justify a derogation the available data shall be from all relevant compartments and not a single (most relevant) compartment, as proposed by the Dossier Submitter.”*

To summarise the analysis (ECHA, 2020), *“although each of the scenarios evaluated presents their own advantages and disadvantages, there is no scenario that addresses all of the identified uncertainties. Nevertheless, it appears that scenario ‘all compartments requirement at G4/G5’ would satisfy the key concern raised during RAC’s evaluation of the Dossier Submitter’s proposal whilst remaining practical and would avoid that a material could be demonstrated as biodegradable in one compartment whilst remaining persistent for long periods in another (and thus contributing to the microplastic concern).”* This approach recognizes that simulation testing may not be practical at the moment for testing MP. To use either ISO test systems or simulation testing brings flexibility. However, RAC noted that this scenario still does not address all of the uncertainties identified. In reality this is never going to occur which is why weight of evidence from other sources including monitoring should be used in persistence assessments. In effect legislation like the EU Water Framework Directive is designed to provide a safety net for chemical safety assessment although this is rarely recognized. It becomes more important in cases where chemicals assessments are challenging.

In terms of appropriate test material, RAC supports the Dossier Submitter’s (ECHA) proposed approach and emphasizes the importance of ensuring an adequate characterization of biodegradability when test materials are comprised of blends of different polymers.

All of these discussions may be more or less applicable to polymer persistence assessment as well. Further research is also necessary on applicability to liquid non water soluble polymers, or resins, etc.

Conceptual framework by ECETOC

A general outline for polymer (bio)degradation assessment has been presented by ECETOC (ECETOC, 2020). This conceptual framework should be considered as ‘living proposal’.

The assessment is based on a tiered approach:

- Tier 0: Identification of the testing needs
- Tier 1: Screening in aqueous medium (including ready biodegradability tests and inherent biodegradability tests)
- Tier 2: Screening test using different test media (marine and freshwater, sediment, soil)
- Tier 3: Simulation biodegradation testing in relevant environmental compartments
- Tier 4: Weight-of-evidence (WoE) evaluation to substantiate absence of persistence

Following all tiers in the sequence described will not be appropriate for all types of polymers and all intended uses. Depending on the type of polymer and its intended use, testing can start and end at any appropriate tier / sub-tier (ECETOC, 2020).

The approach starts with an assessment and identification of relevant morphological and structural descriptors and physico-chemical properties, which is necessary to select appropriate test methods and testing strategy. The following sequence of test systems is similar to the microplastic biodegradation assessment scheme presented before. First the screening tests are used, and after that the simulation tests. The polymer specific (ISO) test methods are integrated in-between supplemented with ASTM methods or OECD TG 306.

The presented framework also includes adaptation of the screening tests such as extension of the test duration due to bioavailability issues, enlargement of test vessels, and recognition that the 10-d window should not apply. All of these adaptations are similar to modified or enhanced ready tests. For this reason, Tier 1 includes specifically the enhanced ready test methods. However, it is also suggested to pre-expose the inoculum if indicated by use. This is usually not accepted for P assessment even for single substances, and it is questionable if it should be accepted for polymers. It can be accepted in specific cases for risk assessment. It could provide additional valuable data for polymers where it is assumed that bioavailability is responsible for limiting biodegradation. If pre-exposure increases biodegradation this would imply other factors other than simply bioavailability are playing a role. For the tier 2 test systems, degree of biodegradation should be assessed in relation to reference material comparable in form, size and surface area.

It is also mentioned to ensure that all testing is relevant. If a polymer product does not enter a given environmental compartment, simulation biodegradation testing in the corresponding compartment is unlikely to provide relevant data that will be used for hazard or risk assessment (ECETOC, 2020). Testing considerations includes availability of relevant substance (i.e. is polymer available without any additives/stabilisers), mechanism of dosing (including preparation of solids to a defined particle size) representative radiolabeled material, adequate analytical methods, mass balance, and extension of test duration.

The approach is finished using a weight-of-evidence where all available physico-chemical information and (bio)degradation data shall be considered. This includes also abiotic degradation, including information on fragmentation and disintegration. Where possible results for synthetic polymer being investigated should be compared with information of similar naturally occurring polymers.

Based on the discussion and considerations made within this report, the ECETOC conceptual framework (ECETOC, 2020) leaves room for improvements with regard to persistence assessment of polymers. It is obvious, that fragmentation and disintegration is an important degradation pathway of polymers, which is considered in the framework as part of the WoE step. This also includes weathering and other types of abiotic degradation which have significant influence on the overall persistence of polymeric products but are not currently included in standard persistence assessments. However, as mentioned in the standard approach for P assessment, if primary degradation is observed it is necessary to identify the degradation products and to assess whether they possess PBT/vPvB properties. This results in the requirement to evaluate all possible fragments or transformation products. However, often the analysis require to identity of all fragments is not feasible. For this reason fragmentation and disintegration should only be used for P assessment if it is clear that all transformation products will result in no additional concern (i.e. over and above that of the parent polymer) as well. In principle, if a parent polymer molecule undergoes a primary transformation, often the transformation products will have a similar degradation rate as the parent (i.e. essentially smaller fragments of the parent polymer). Exceptions could be if the polymer contains reactive functional groups, which react first leaving a less degradable structure behind. This could be deduced by considering the polymer structure and functionality. In each case there will need to be case by case evaluations of the polymer structure, primary degradation and subsequent transformation products. In this approach it is important to note that in many cases theoretical/computational methods will be needed as it will almost certainly not be feasible or practical do undertake all this work experimentally.

Where ever possible, this conceptual framework recommends the inclusion of a comparison and benchmark to natural polymers as a weight-of-evidence to show that the (modified or synthetic) polymer substance will have no 'unacceptable persistence' (i.e. significantly more persistent than similar naturally occurring polymers). This implies that natural polymers will have an acceptable persistence which is the subject which needs to be further addressed. As shown above, although data are limited, it is expected that many natural polymers do not pass the criteria for persistence given in Annex XIII of the REACH regulation (EC, 2011) and certainly not for all compartments. These natural polymers may not have a concern, i.e. they will have an acceptable persistence, only by considering further properties (e.g. bioavailability, toxicity, etc). Therefore, even if the degradation potential (degradation rate) is comparable for the modified/synthetic polymer and the natural polymer, evidence is required to demonstrate that their other properties are similar as well to ensure a valid comparison. Further research is needed what is an acceptable persistence.

ASTM approach

In 2018 ASTM published a "Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation"(ASTM, 2018). This guide provides a framework or road map to compare and rank the controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal and photooxidation processes as well as the biodegradation and ecological impacts in defined applications and disposal environments after degradation (see **Fehler! Verweisquelle konnte nicht gefunden werden.** D6954-18). This approach was applied by Meereboer et al. (2020) together with other information to review biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites.

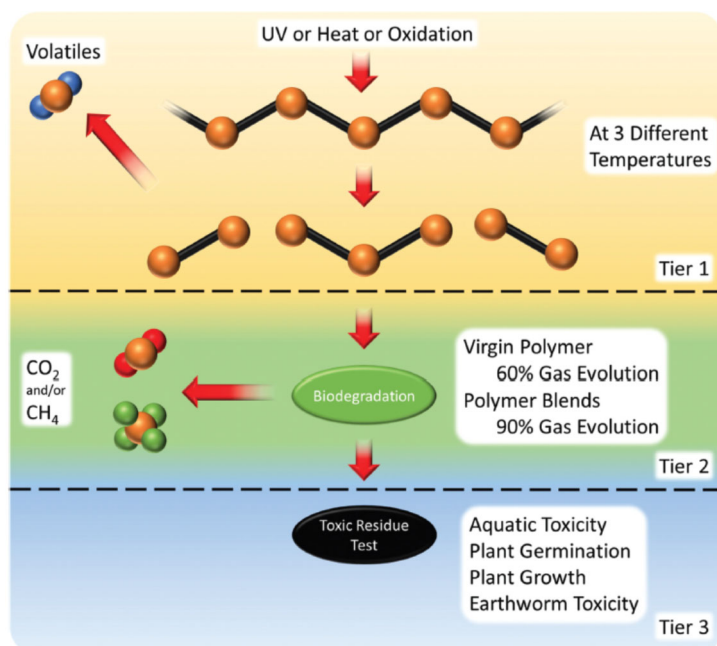


Figure 4: ASTM D6954-18 oxidation and biodegradation standard test procedure (taken from Meereboer et al. (2020))

This approach considers pre-treatment of the neat polymeric material before applying it in the biodegradability test and/or use tests that combine multiple processes. Another option is to perform the test separately, and identify in a first step the transformation products within the weathering test system, and in a second step evaluate the relevance of the identified transformation products by QSAR or experimental investigations.

This approach illustrates most impressive that many of the polymers cannot follow standard chemical persistence assessment approaches and often needs a stepwise approach to include further processes. However, justification for this approach is needed case by case in the weight of evidence approach if this stepwise approach is applicable for the specific polymer.

Polymer of low concern (PLC), Polymer requiring registration (PRR), and Reduced Regulatory Requirement (RRR)

In 2009, the OECD published an analysis of the polymer of low concern (PLC) concept (OECD, 2009) and the criteria of PLC have been discussed and agreed. Polymers of low concern (PLCs) are "those deemed to have insignificant environmental and human health impacts. Therefore, these polymers should have reduced regulatory requirements." This concept has been applied under different regulatory settings. Thereby, it will often be discussed if biodegradable, non-persistent polymers should not be regarded as polymers of low concern, due to resulting in more bioavailable fractions, and thus potentially need to meet chemical registration requirements. The term 'polymers requiring registration' (PRR) is used to indicate those polymers that could be candidates for future registration under the REACH regulation (Wood, 2020). However, biodegradability is not a proposed criteria, and in this report it is stated that "it cannot be stated that 'non-PLC = PRR', which is also pointed out in the ECETOC conceptual framework for polymer risk assessment (ECETOC, 2019)".

In Canada, one of the criteria in determining whether a polymer qualifies as an Reduced Regulatory Requirement (RRR) polymer is whether it is designed or expected to "substantially degrade, decompose or depolymerize" (Government of Canada, 2021). If there is evidence that the polymer will degrade, transformation products should be identified and information concerning their hazard should be gathered. In silico method can be used to give evidence since experimental information is often not

available. If the transformation products of a polymer are of low hazard, it may qualify as an RRR polymer, despite degrading, decomposing or depolymerizing, depending on whether other criteria are met (Government of Canada, 2021).

Taking this in account it seems reasonable for polymers, if they are considered to be PRR, that the persistence assessment should be more target-oriented, for example in the context of a PBT assessment to focus on fragments or transformation products which will have additionally bioaccumulative and/or toxic properties and not assess all transformation products in detail on their persistence as would currently be recommended by the standard approach.

The pilot project report on the grouping of EPDLA polymers identified PLC based upon hazard similarities taking into account the presence of high or medium concern reactive functional groups (RFG) as defined under the Canadian PLC scheme (EPDLA, 2021). It has been hypothesized that comparison with criteria from Wood PFA report (Wood, 2020) indicate that a large number of polymers would be identified as PRR in Europe and PLC elsewhere.

Assessment approaches for UVCB

As mentioned above the issue with P assessment of polymers are often based on the complex and variable composition. In contrast to UVCBs, where the constituents are often partly unknown, polymers having some variability but being of known composition (ECETOC, 2021). Nevertheless, approaches used for UVCB may also be applicable to polymers.

To evaluate PBT properties of substances containing multiple constituents, impurities and/or additives, assessment approaches have been described in the REACH guidance R.11, chapter R.11.4.2.2.2 (ECHA, 2017b). This includes

- Known constituent approach
- Fraction profiling (or Block profiling) approach
- Whole substance approach

A short overview is given here, for details refer to the R.11 guidance (ECHA, 2017b). In the known constituent approach all known constituents of the substance will be evaluated separately. Depending on the number of known constituents a high number of tests are necessary. In the fraction profiling approach the substance is divided into different fraction of similar properties. In this case all of these fractions will be tested as a whole, or a representative constituent for each of the fractions. In the third approach the whole substance will be tested. Thereby each of these approaches have their advantages and disadvantages. Often a combination of these approaches is necessary to decide on the best assessment strategy.

Generally, these approaches may be applicable to (some) polymer types, but the most suitable approach has to be evaluated accurately. Often the known constituent approach may not be applicable due to the high number of constituents, especially if potential transformation products are taken into consideration. On the other hand the whole substance approach is often also not applicable for persistence assessment due to minor constituents which may be persistent. For this reason a target-oriented evaluation of the profiling of the substance is needed to decide on specific fractions of concern and potential representative key constituents (worst-case constituents).

In comparison to most known UVCB substances the composition of polymer (products) may be more tightly defined. This does not mean that they do not vary, but the constituents in the substance are very similar, i.e. molecules with very different molecular weight but very similar subfractions. For this reason the substances will often result in similar transformation products and in the extreme case be the monomers. This gives the possibility to decide on suitable fractions with representative key

constituents and the read-across to further constituents in each of the fractions. For this reason the fraction profiling approach seems to be the most promising approach for most polymers. However, depending on the profiling, the other approaches or a combination thereof may be suitable in specific cases.

In a pilot project Epoxy Europe evaluated the grouping of epoxy polymers (Epoxy Europe, 2021). The epoxy polymers are (partly) insoluble polymers and thus the existing test methods are not well suitable for the whole substance. In this project Bisphenol-A-Diglycidylether (“BADGE”) has been identified as key constituent in BADGE epoxy resin polymers for hazard and risk assessment. All polymers of the group contain a variable ratio of BADGE, which is also a registered substance with full dataset.

Nevertheless a sufficient justification of the approach used is necessary, considering all available information, i.e. for example available information on single constituents even if the whole substance approach is used and vice versa. This justification should be used to justify the approach taken and contain a discussion of remaining uncertainties and limitations.

5 Conclusion

Polymers are a diverse substance group with a wide range of classes or types and properties and many of these properties will be intrinsically linked to their environmental fate. An evaluation of the degradation potential and persistence of polymers is essential to assess the probability on long-term presence and accumulation in the environment. The assessment of the environmental hazard and fate properties of polymers is associated with considerable challenges that go beyond the assessment of individual substances. The nature of a polymer having multiple components drives the determination of all structural and morphological descriptors and physico-chemical properties, and it is necessary to identify those properties, that make a difference for degradation potential. However, the complex and variable nature of the different types of polymers creates difficulties in developing one standardised approach for all polymers.

To summarize, a potential framework on persistence assessment of polymers should consider several information and building blocks which have been derived based on the evaluation of the standard P assessment approach as described for the PBT assessment under REACH and its applicability to polymers, as well as on the evaluation of alternative test systems and methodologies developed for polymeric materials. Further aspects to be considered are the result of the understanding of biodegradation potential of natural in comparison to synthetic polymers,

Usually several screening and assessment information shall be considered for the persistence assesment using a weight-of-evidence approach. Different challenges for polymers have been discussed above using the given **standard approach and test systems**.

Simulation test systems (OECD TG 307, 308, 309)

Performing adequate simulation test systems is challenging, as the characteristics of polymers make robust measurements difficult in these test systems. In addition, challenges exist with the potential high number of transformation products. The challenges can be summarized as follows:

- Application rates of the test substance to the test compartment
- Availability of appropriate analytical methods (for both whole substance and transformation products)
- Synthesis of radiolabelling material
- Mass balance and recovery
- High number of transformation products (identification and separate evaluation needed)

For these reasons, only a limited number of simulation tests are available for polymers up to now. In addition, RAC highlighted the practicality and applicability of simulation test methods to microplastic test materials (ECHA, 2020).

Screening test systems (ready, modified, enhanced and inherent biodegradability test systems)

Screening and testing using indirect parameters such as O₂ consumption or CO₂ evolution, i.e. mineralization, might be a better choice. However, this screening is often not suitable, as it is unclear if all components have been degraded. In addition, polymers typically consist of large molecules, which are even mostly solid and insoluble in water, whereby the bioavailability is reduced, and thus often polymers will not meet the criteria of screening test systems. Again, the challenges can be summarized as follows:

- Difficult to adequately quantify ThOD or ThCO₂ of polymers
- Due to sequential biodegradation, 10-day-window criteria not applicable
- Applicability of the pass/fail criteria
- Limited bioavailability
- Test duration

In conclusion, available results of screening test systems should be interpreted carefully, and evidence for reliability is needed as well as a reflection on the biodegradability of all constituents.

Moreover, abiotic degradation (hydrolysis and photodegradation) plays a major role in the weathering of polymers/plastics and their degradation. This weathering often represents an initially required step for further biodegradation of the polymeric material.

Overall, the standard approach and test systems for chemical persistence assessment are not necessarily applicable to all types of polymers, but may be applicable to specific groups of polymers such as water soluble polymers. However, similar limitation still arise as for UVCB such as: (i) it does not make sense to apply the 10 day window criterion in ready biodegradability test systems, (ii) different degradation kinetics for different constituents are expected. In the end, the issues for persistence assessment of polymer with the standard approach could be attributed and categorized on three facts/properties which is illustrated in Figure 5.

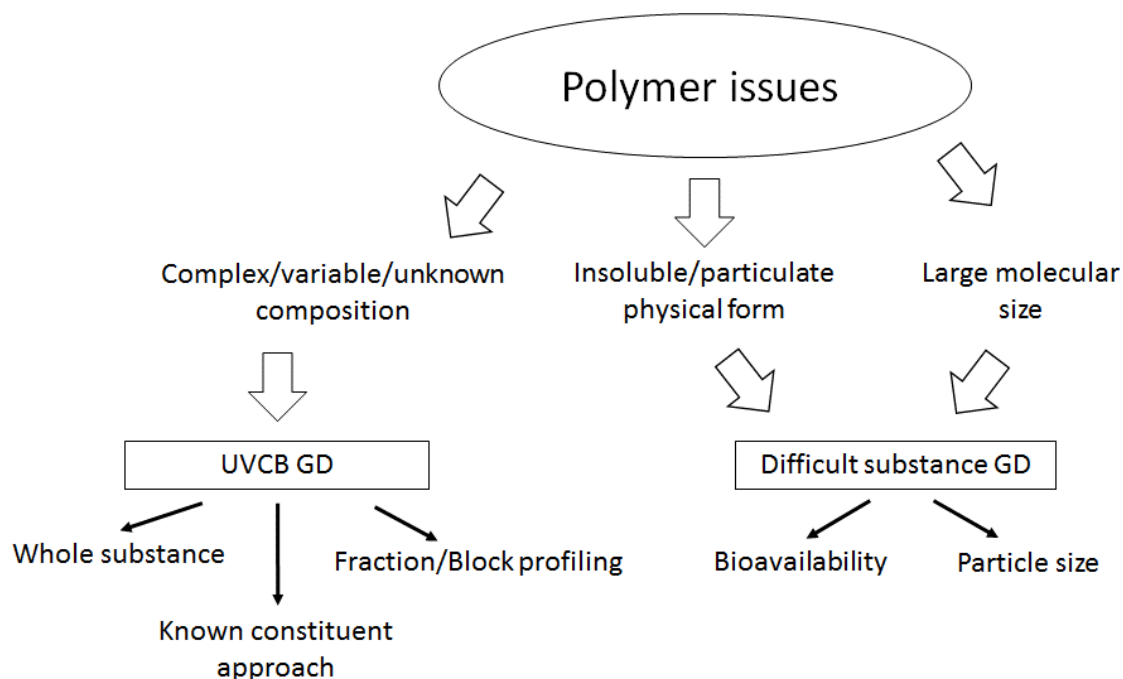


Figure 5: Categorization of the polymer issues with the standard approach and test systems

To deal with these issues **special test systems and approaches** have been developed for polymers. Some points are addressed by **ISO guidelines** for testing the (bio)degradation of polymers.

- Increased bioavailability by recommendation to test powder (< 250 µm)
- Test duration
- Benchmarking to reference substance

These test systems can be regarded as in-between the enhanced biodegradation test systems and the simulation testing. The test guideline for aqueous medium is even comparable to an enhanced

biodegradation test system. Comparable to the standard screening test systems they usually follow the degradation via indirect parameters such as O₂ consumption or CO₂ evolution, i.e. mineralization. By doing so they will overcome the analytical challenges of the simulation testing, but the same limitations as for the ready biodegradability test systems as well as the enhanced or inherent test systems exist. However, they should still be regarded as screening test systems only. Please note, test systems on anaerobic degradation, sewage treatment plant simulation (STP), or composting, which are using often finished articles, are considered only as supporting information with regard to the persistence assessment.

For the persistence assessment of the polymer we have to differentiate between polymeric substances and plastic materials or articles. To assess persistence of the substance only the property of the polymeric substance may be relevant, and not the biodegradation of for example a film or plastic sheet. Considering this the polymeric substance could be biodegradable and thus not persistent, but the article will notwithstanding be present in the environment after emission for a relatively long time (i.e. environmentally persistent). This is similar to natural polymers such as wood (material, object), for which the degradation will be longer than for the polymer (substance) cellulose or lignin. Thereby the bioavailable fraction is the critical characteristic which is limited by the surface area. In a first step, bulk and surface erosion is used for breaking the material in smaller pieces. These smaller pieces can then be sufficiently attacked by microorganisms (enzymatic hydrolysis). For this reason, for persistence assessment of a polymeric substance a solid polymer should probably be tested as small as possible without affecting the actual structure of the polymeric substance. Such an increasing of the bioavailability is also accepted for single substances (ECHA, 2017a; ISO, 2018a; OECD, 1992). In conclusion, for biodegradation studies the polymer should be tested with standard form and shape, probably as a powder (< 250 µm as recommended by the ISO standard guidelines). Thereby any change of substance (structure) by milling will have to be excluded. However, this recommendation is only to assess persistence of polymeric substances in standard tests and not to be confused with testing biodegradability of materials (plastic articles, films) under real environmental conditions.

In addition, some **non-guideline tests** have been described in literature. These non-guideline tests often follow the degradation by measuring unspecific parameters or the functionalities, and thus are often regarded only of limited relevance for persistence assessment. However, they indicate that material or substance properties have altered, and they could potentially be used to get supporting information on degradation pathways or potential fragments or even transformation products, and to decide on further testing strategy. Beyond that, some non-guideline studies provide promising approaches such as alternative endpoints. These can be used to develop new testing approaches or adapt the existing guidelines to polymers. Another option is to use field/mesocosm studies to consider real environmental conditions. However, as mentioned above these are usually no closed systems, and thus not all relevant information on transformation products is available. Even if these test systems give beneficial information on the fate of a plastic article, the utility for the persistence assessment of the polymeric substance is limited. Sufficient justification is necessary if such tests are used in the weight-of-evidence approach, especially on how results about fragmentation or degradation of the plastic article, add to the knowledge about the degradation of the polymeric substance.

It is apparent that the majority of tests and test schemes for polymers miss the importance of **weathering** on the degradation rate of polymers. Environmental weathering by sun-light (UV) or heat promotes formation of C-O bonds, which promote disintegration and fragmentation of the polymer. The effect of sunlight could be considered separately to the biodegradation testing, or in a pre-treatment step to the neat polymeric material, and combine these multiple processes in a step wise assessment. However, even if extensive weathering occurs there is no guarantee of subsequent biodegradability of the fragments. Besides the photodegradation, hydrolysis is often the primary step

of polymer degradation, resulting in wettability of the polymer as an important influencing factor. Thereby the polymer particles may be degraded by surface erosion or bulk erosion. Both, photodegradation and type of hydrolysis, will have an influence on the testing strategy for persistence assessment and on selecting an adequate analytical method. Nevertheless, abiotic degradation data may not be used on their own within persistence assessment, but only as part of a Weight-of-Evidence approach. If we take for granted that abiotic degradation is the primary degradation step, the resulting information about transformation products (or fragments) can be used in a testing strategy focussing on the identified components (material) as preferred compounds for further biodegradation testing. If corresponding studies indicate that these fragmentation products are persistent on their own (and more bioavailable due to the lower mass), the whole polymer can be regarded as having concern. If these fragments have no concern, the abiotic degradation rate (kinetic) is important to be evaluated for relevance on environmental conditions.

Finally, several **approaches and methodologies** (for biodegradation testing and assessment) have been presented in the literature which are (partly) applicable to the persistence assessment of polymers.

- In the RAC opinion for restriction of microplastic (ECHA, 2020), the Rapporteurs together with an ad-hoc RAC working group developed a series of eight scenarios comprising different approaches to the tests considered necessary to justify a derogation from the proposed restriction.
- A general outline (conceptual framework) for polymer (bio)degradation assessment has been presented in the ECETOC technical report No. 133-2 (ECETOC, 2020). Both concepts integrate the ISO standards in the assessment scheme, and provide guidance for interpretation.
- The ASTM approach integrates weathering in a tiered approach to assess biodegradation in the marine environment.
- Further approaches have been discussed during the development for polymer of low concern (PLC) and polymer requiring registration (PRR).
- Assessment approaches have been described in the REACH guidance R.11 (ECHA, 2017b) to evaluate PBT properties of substances containing multiple constituents, impurities and/or additives (chapter R.11.4.2.2). These approaches may be applicable to (some) polymer types, but the best suitable approach has to be evaluated accurately. Often the known constituent approach may not be applicable due to the high number of constituents, especially if we consider potential transformation products. The whole substance approach is also often not applicable due to (unknown) minor constituents which may be persistent.

In conclusion, at the beginning a target-oriented evaluation of the profiling of the substance is needed to decide on specific fractions of concern and potential representative key constituents. This seems to be the most promising approach for most polymers. However, depending on the profiling, the other approaches or a combination may be suitable in specific cases as well. A combination of all approaches seems to be most appropriate. As a consequence for each polymer evidence is needed on the applied approach case by case.

5.1 Key Findings

Overall, persistence assessment of polymers is challenging. The evaluation within this research on available information on (bio)degradation of polymers, on the current standardization and the methodologies will be a useful source for the development of a new framework for persistence assessment of polymers. Key findings are:

- Polymers may require registration under REACH as part of the EU Chemicals Strategy for Sustainability
- High variability of polymer types and properties so that one approach/framework will not be suitable to address all types of polymers.
- Natural polymers are considered as sufficiently biodegradable, having no concern for the environment, and thus they are not subject to persistency assessment. Many natural polymers have to be regarded as P/vP if the REACH Annex XIII criteria will be applied. 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.
- 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).
- Weathering (by Heat, Water, UV) is an important process in (bio)degradation of polymers as it is often the initial step of degradation, and thus should be considered in the framework at least in the development of the testing strategy and the weight-of evidence.
- Current standard approach for assessing persistence within the PBT assessment under REACH is considered unlikely to be applicable to all polymers (but probably applicable to few specific polymers) – adaptation will be needed
- Polymer specific guidelines are available (e.g. ISO standards for testing biodegradation of plastic materials). These test systems can be regarded as comparable to enhanced biodegradation test systems or in-between the enhanced biodegradation test systems and the simulation testing. However, they should still be regarded as screening test systems only.
- For persistence assessment of polymeric substances (not plastic materials or articles), the polymer should be tested using standardized methods with standard form and shape, probably as a powder (< 250 µm as recommended by the ISO standard guidelines).
- Results from non-guideline tests are often regarded only of limited applicability for persistence assessment and thus are used only as supporting data, but some non-guideline studies provide promising approaches such as alternative endpoints.
- Different approaches and methodologies have been presented in the literature to overcome the challenges with polymers. Based on an accurate profiling of the substances the best approach should be selected; a combination of the methodologies is most promising.

5.2 Framework on Persistence assessment of Polymers

The framework to assess persistence of polymers should include several building blocks and follow a stepwise approach:

Step 1: Collect and assess available information

- a. Specification (“Profiling”) of the polymer
- b. Identification and evaluation of existing information on (bio)degradation

Step 2: Evaluate applicability of methodologies

- a. Reduced Regulatory Requirements
- b. Standard assessment approach
- c. UVCB approaches and ASTM approach

Step 3: Problem formulation

Step 4: Select approach, testing strategy and evaluate persistence

- a. Select and justify the approach
- b. Select testing strategy and noting limitations
- c. Evaluate relevance of transformation products

Finally, prepare Weight-of-Evidence (WoE) for persistence assessment of the polymer based on the available information and justifications.

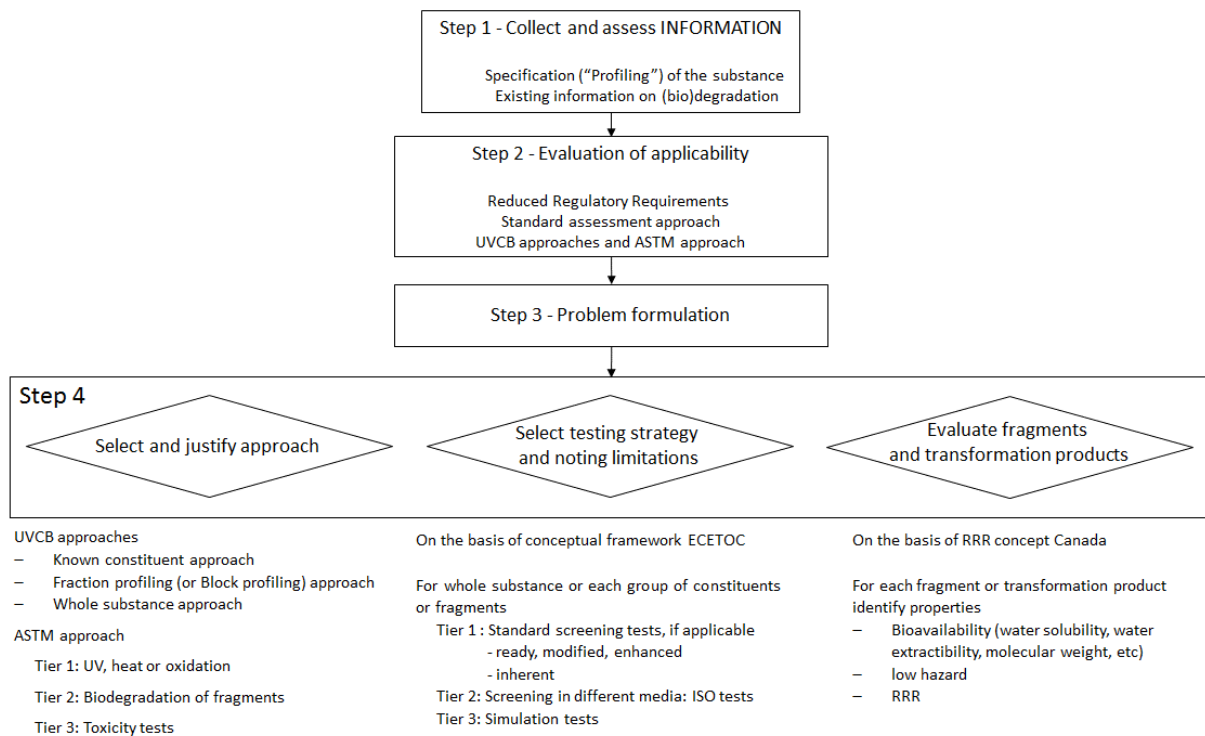


Figure 6: Flow diagram on the persistence assessment of polymers

5.2.1 Specification (“Profiling”) of the polymer

In a first step, the polymer should be described and specified as far as possible. Thereby relevant morphological and structural descriptors and physico-chemical properties should be identified:

- Information on (structural) identity as far as possible; relevant functional groups, molecular weight
- Information on morphology: form, shape, size
- Physico-chemical properties such as water soluble or solid, density, crystallinity, wettability

Please note that under REACH a polymer substance include (a) additives such as stabilizers, (b) impurities such as catalysts residues, and (c) unreacted monomers. In contrast, other additives such as pigments, lubricants, thickeners, antistatic agents, antifogging agents, nucleating agents and flame retardants are part of the material.

Based on this information a first draft should be developed for grouping of the constituents in fractions of similar properties with regard to (bio)degradation, and representative key constituents should be identified for each fraction.

5.2.2 Identification and evaluation on existing information on (bio)degradation

In the second step, all available information on existing (bio)degradation studies should be gathered. This includes information on representative key constituents (as identified in step1), as well as on fractions or the whole substance.

In detail following information is of interest:

- (a) Abiotic degradation studies
 - Hydrolysis
 - Photooxidation
 - Weathering, disintegration/fragmentation/persistence of length
- (b) Biodegradation studies (
 - Simulation tests (OECD 307, 308, 309)
 - OECD screening tests (OECD 301, 310, modified, enhanced, 302, 306)
 - ISO tests
- (c) Other information which might be useful for a weight of evidence approach
 - Non-guideline tests on biodegradation
 - Tests on composting and simulation test in sewage treatment plants
 - QSAR predictions
 - Information about distribution in the environment
 - Bioavailability
 - Field/mesocosms tests
 - Field monitoring data if available

Evaluate if the available information is reliable with regard to the (bio)degradation of the substance or any group (fraction) of the substance in the sense of P assessment.

5.2.3 Evaluation of applicability of approaches

Based on the information from step 1, in this step it should be evaluated the applicability of the

- Reduced Regulatory Requirement (RRR)

- Standard approach including the standard test systems
- UVCB approaches, and ASTM approach

Considerations:

- Hypothesis of degradation pathway of whole substance, fractions, and key constituents based on structural and morphological information; bioavailability; fragments by weathering; expected transformation products
- Evaluate influence and relevance of results from standard test systems on reliability
- if biodegradation rate of constituent (groups) are expected to be significant different, refine draft grouping

The result will be used to prepare a justification if the polymer (and where applicable potential fragments or transformation products) meet the Reduced Regulatory Requirement (RRR), and if the standard approach is applicable for the substance or any group (fraction) of the substance in the sense of P assessment. Summarize reasons/challenges/limitations to develop suggestions for adaptation of testing.

5.2.4 Problem formulation

Based on the information from step 1 and 2, the hypothesis should be formulated in detail which has to be answered by the following selection of approaches and testing strategy. This can be the question on the persistence of the whole polymer or of specific fractions or group of constituents which have the most impact on the persistence of the whole substance.

The aim should be to conclude on persistence with the least possible efforts in testing and at the same time cover the assessment of persistence in all environmental compartments (marine water, fresh or estuarine water, marine sediment, fresh or estuarine sediment and soil).

For this reason, in a first step, the fraction or group of constituents should be selected with the highest likeliness to affect the persistence of the whole substance, fragments or transformation products.

5.2.5 Select and justify approach

To get evidence on the evidence different approaches are available. Based on the “profiling” above select which approach is appropriate for which group (fraction) of constituents similar as for UVCB

- Known constituent approach
- Fraction profiling (or Block profiling) approach
- Whole substance approach

Often a combination of these UVCB approaches is necessary depending on the already available information.

In addition, the ASTM approach recommends to check in tier 1 which fragments will be formed under weathering conditions. These fragments will be regarded as having a higher concern for the environment. For this reason, these fragments should be tested in tier 2 for biodegradation potential (and toxicity).

On the basis of this approach the testing effort may be reduced on the most relevant fragments for the environment. If it can be concluded that these fragments are persistent, the whole polymer can be considered as persistent, and has not to be tested independent on the applicability of standard

approaches. However, this approach is only possible if the fragments are available (by considering pre-treatment (UV, heat))

5.2.6 Select testing strategy and noting limitations

Develop testing strategy for (bio)degradation testing per fraction or representative key constituent using application or adaptation of OECD guideline studies as well as ISO test systems.

Evaluate which are the most appropriate test system for which fraction, or key constituent:

- Standard screening test systems including ready biodegradation test system (OECD 301, 310), enhanced biodegradation test system, or inherent biodegradation test system (OECD 302)
- Screening test systems using different media (including OECD TG 306, and ISO test systems)
- Simulation testing systems (OECD 307, 308, 309)
- Other test systems and non-guideline test systems (mesocosms/field)

Testing considerations:

- Degradation pathway: weathering, disintegration/fragmentation, wettability, hydrolysis (surface or bulk erosion), mineralization
- Should pre-treatment steps be considered for neat polymers, and/or use tests that combine multiple processes.
- Testing material: standard form and shape film, powder, powder < 250 µm as mentioned in ISO guidelines; change of substance identity (see profiling above) by milling have to be excluded
- Analytical method, endpoint
- Surface degradation rate, normalization

5.2.7 Evaluate relevance of fragments or transformation products

In this step, use information from available biodegradation tests and new information which fragments (e.g. after weathering) or transformation products are formed, and evaluate relevance of these fragments or transformation products by:

- Identify properties of fragments or transformation products; use if experimental data are not available in a first step in-silico approaches (QSAR, etc)
- Check bioavailability (important for biodegradation potential, bioaccumulation and toxicity) of fragments or transformation products
- Focus/limit on fragments or transformation products of increased concern for P(BT)
- Would fragments or transformation products meet RRR? If so justify that assessment approach can stop at this point
- If do not meet RRRs prepare testing strategy for relevant (group of) fragments or transformation products

5.2.8 Weight-of-Evidence for Persistence assessment of the Polymer

This part of the framework is the documentation and communication of the persistence assessment. Prepare report about the outcome of the persistence assessment of the polymer including justification on testing strategy.

Essential elements (based on the workflow above):

- Profiling of the substance
- Available information on biodegradation using the standard assessment scheme and/or evaluation on applicability of standard assessment scheme
- Available information on polymer specific guidelines, and non-guideline studies
- Impact of weathering on disintegration/fragmentation. Are potential fragments formed which could be a concern for the environment. Has this fragmentation an influence on the profiling of the substance
- Select approach and structure the information based on the profiling/approach selected (known constituent approach, whole substance approach, or fraction profiling). Can key representative be given per fraction
- Evaluate persistence of each fraction and for the whole substance; consider relevant transformation products

Use the guiding principles published by OECD (OECD, 2019), and the **ECHA template**³ for weight-of-evidence to structure the information:

- Problem formulation
- Information on degradation per fraction
- Level of confidence and uncertainty

Especially the tables of the template are helpful to illustrate the available data, as well as the confidence and uncertainty of a justified and not justified conclusion on persistence of the polymer.

³ <https://echa.europa.eu/de/support/guidance-on-reach-and-clp-implementation/formats>

5.3 Further research needs

The framework described above uses available published information on methodologies on polymer (bio)degradation and persistence assessment. In these methodologies, the persistence criteria developed for PBT assessment of organic single substances have been taken as given (specified in Annex XIII (EC, 2011)). However, applicability of these criteria to particulate materials, and to the microplastic concern specifically, is less certain (ECHA, 2020). Over the years, scientific understanding of polymer degradation has increased, but there are still significant knowledge gaps, especially when compared with natural polymers. Many natural polymers would fulfil the P/vP criteria (which actually don't apply), but are considered having no concern for the environment. 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. This also needs to be recognized when assessing synthetic polymers. For such polymers it would also be important to establish polymer specific criteria to enable an adequate hazard or safety assessment. Finally, the assessment would benefit from an agreement and accepted definition regarding when a polymer (and where applicable potential transformation products) meet the Reduced Regulatory Requirements (RRRs).

In conclusion, uncertainty still exists and following further research is advisable.

ECHA RAC recommends that additional research is undertaken to further explore and understand (ECHA, 2020):

- the environmental relevance of the 'relative to reference material' based test methods included in group 4 (ISO test methods);
- the practicality and applicability of group 5 (simulation) test methods to microplastic test materials and, more generally;
- the applicability of REACH Annex XIII half-life criteria to particulate materials.

In addition, the evaluation within this project (CEFIC LRI Eco52) shows that following further points should be investigated in more detail:

- Testing of biodegradation / persistence
 - Improved guidance on polymer dosing
 - Acceptability of non-standard tests to assess polymer persistence (e.g. mesocosms)
 - Similarity of condition of weathering in ISO tests to OECD photolysis guidelines, and acceptability of such pre-treatment within persistence assessment
- Relevance of test results
 - Environmental relevance of the limit of particle size (< 250 µm) within biodegradation testing
 - Surface normalized degradation rates or SDR and comparison of these values to standard half-lives
 - Is the degradation of the polymer including the stabiliser (polymer product) the degradation of the material rather than degradation of the substance?
 - Take polymer particles not as macromolecule (substance) but as material with a certain crystallinity
 - How to assess the time scale of sequential transformation processes and its relevance for hazard and risk assessment

- Persistence assessment methodologies
 - Applicability for water soluble polymers
 - Applicability for liquid non water soluble polymers
 - Applicability for polymer resins
 - How to assess and evaluate bioavailability? Consideration of bioavailability in the persistence assessment approach?
- Relevance of P and vP criteria to polymers when many naturally occurring polymers meet these criteria?
 - Would inclusion of natural polymer to benchmark be appropriate? Which one?
 - How can all compartments be evaluated?
 - What is an acceptable persistence?
 - Development of criteria when polymers fulfil the reduced regulatory requirements (RRR)
- How to connect persistence with sustainability criteria that include factors such as resource efficiency or product life ?

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7 References

- Albright, V.C., 3rd, Chai, Y., 2021. Knowledge Gaps in Polymer Biodegradation Research. *Environ Sci Technol* 55, 11476-11488.
- Allen, S., Allen, D., Moss, K., Le Roux, G., Phoenix, V.R., Sonke, J.E., 2020. Examination of the ocean as a source for atmospheric microplastics. *PLoS One* 15, e0232746.
- Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., Galop, D., 2019. Atmospheric transport and deposition of microplastics in a remote mountain catchment. *Nature Geoscience* 12, 339-344.
- Andrady, A.L., 1994. ASSESSMENT OF ENVIRONMENTAL BIODEGRADATION OF SYNTHETIC-POLYMERS. *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics* C34, 25-76.
- Andrady, A.L., 2011. Microplastics in the marine environment. *Mar Pollut Bull* 62, 1596-1605.
- Andrady, A.L., 2017. The plastic in microplastics: A review. *Mar Pollut Bull* 119, 12-22.
- Arcos-Hernandez, M.V., Laycock, B., Pratt, S., Donose, B.C., Nikolić, M.A.L., Luckman, P., Werker, A., Lant, P.A., 2012. Biodegradation in a soil environment of activated sludge derived polyhydroxyalkanoate (PHBV). *Polymer Degradation and Stability* 97, 2301-2312.
- ASTM, 2018. ASTM D6954-18 - Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation.
- Bernhard, M., Eubeler, J.P., Zok, S., Knepper, T.P., 2008. Aerobic biodegradation of polyethylene glycols of different molecular weights in wastewater and seawater. *Water Res* 42, 4791-4801.
- Briassoulis, D., Dejean, C., 2010. Critical Review of Norms and Standards for Biodegradable Agricultural Plastics Part I. Biodegradation in Soil. *Journal of Polymers and the Environment* 18, 384-400.
- Briassoulis, D., Mistriotis, A., Mortier, N., Tosin, M., 2020. A horizontal test method for biodegradation in soil of bio-based and conventional plastics and lubricants. *Journal of Cleaner Production* 242.
- Brueckner, T., Eberl, A., Heumann, S., Rabe, M., Guebitz, G.M., 2008. Enzymatic and chemical hydrolysis of poly(ethylene terephthalate) fabrics. *Journal of Polymer Science Part A: Polymer Chemistry* 46, 6435-6443.
- Burgstaller, M., Potrykus, A., Weißenbacher, J., Kabasci, D.S., Merrettig-Bruns, D.U., Sayder, B., 2018. Study on the treatment of biodegradable plastics.
- CESIO, 2021. Pilot project report on the grouping of [polymers] - Alcohol ethoxylates (AEs). <https://circabc.europa.eu/ui/group/a0b483a2-4c05-4058-addf-2a4de71b9a98/library/6c23e389-b6be-48b8-af09-18ee56fe11b2/details>.
- Chamas, A., Moon, H., Zheng, J.J., Qiu, Y., Tabassum, T., Jang, J.H., Abu-Omar, M., Scott, S.L., Suh, S., 2020. Degradation Rates of Plastics in the Environment. *ACS Sustainable Chemistry & Engineering* 8, 3494-3511.
- Chinaglia, S., Tosin, M., Degli-Innocenti, F., 2018. Biodegradation rate of biodegradable plastics at molecular level. *Polymer Degradation and Stability* 147, 237-244.
- Cousins, I.T., Ng, C.A., Wang, Z., Scheringer, M., 2019. Why is high persistence alone a major cause of concern? *Environmental Science Processes & Impacts* 21, 781-792.
- DIN, 2018. EN 17033 - Plastics – Biodegradable mulch films for use in agriculture and horticulture – Requirements and test methods; German version EN 17033:2018.
- Duis, K., Coors, A., 2016. Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects. *Environ Sci Eur* 28, 2-2.
- Duis, K., Junker, T., Coors, A., 2021. Environmental fate and effects of water-soluble synthetic organic polymers used in cosmetic products. *Environ Sci Eur* 33.
- EC, 2006. REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL OF 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94

- as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.
- EC, 2011. COMMISSION REGULATION (EU) No 253/2011 of 15 March 2011 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XIII.
- ECETOC, 2019. The ECETOC Conceptual Framework for Polymer Risk Assessment (CF4Polymers). Technical Report No 133-1. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium, p. 131.
- ECETOC, 2020. Applicability of Analytical Tools, Test Methods and Models for Polymer Risk Assessment. Technical Report No 133-2. European Centre for Ecotoxicology and Toxicology of Chemicals, p. 150.
- ECETOC, 2021. Case Studies Putting the ECETOC Conceptual Framework for Polymer Risk Assessment (CF4Polymers) into Practice. Technical Report No 133-3.
- ECHA, 2012. Guidance for monomers and polymers, Version 2.0. Guidance, vol. Guidance for the implementation of REACH. European Chemicals Agency, Helsinki, Finland, p. 26p.
- ECHA, 2017a. Guidance on Information Requirements and Chemical Safety Assessment Chapter R.7b: Endpoint specific guidance, Version 4.0.
- ECHA, 2017b. Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB assessment Version 3.0 June 2017.
- ECHA, 2020. RAC and SEAC opinion on an ANNEX XV RESTRICTION REPORT PROPOSAL FOR A RESTRICTION for intentionally added microplastics.
- Emadian, S.M., Onay, T.T., Demirel, B., 2017. Biodegradation of bioplastics in natural environments. Waste Management 59, 526-536.
- EPA network - Interest group on Plastics, 2018. Biodegradable Plastics Approaches and experiences from 16 Members of the EPA Network. In: Maier, N. (Ed.), https://epanet.eea.europa.eu/reports-letters/reports-and-letters/ig-plastics_working-paper_biodegradable-plastics.pdf/view.
- EPDLA, 2021. Pilot project report on the grouping of [EPDLA polymers]. <https://circabc.europa.eu/ui/group/a0b483a2-4c05-4058-addf-2a4de71b9a98/library/6c23e389-b6be-48b8-af09-18ee56fe11b2/details>.
- Epoxy Europe, 2021. Pilot project report on the grouping of [EPOXY polymers]. unpublished.
- Eubeler, J.P., 2010. Biodegradation of Synthetic Polymers in the Aquatic Environment. BASF, vol. Dr. rer. nat. . Universität Bremen, Bremen, p. 209p.
- Eubeler, J.P., Bernhard, M., Knepper, T.P., 2010. Environmental biodegradation of synthetic polymers II. Biodegradation of different polymer groups. Trac-Trends in Analytical Chemistry 29, 84-100.
- Eubeler, J.P., Zok, S., Bernhard, M., Knepper, T.P., 2009. Environmental biodegradation of synthetic polymers I. Test methodologies and procedures. TrAC Trends in Analytical Chemistry 28, 1057-1072.
- European Bioplastics, 2018. What are bioplastics? - Material types, terminology, and labels – an introduction.
- Fenner, K., Screpanti, C., Renold, P., Rouchdi, M., Vogler, B., Rich, S., 2020. Comparison of Small Molecule Biotransformation Half-Lives between Activated Sludge and Soil: Opportunities for Read-Across? Environ Sci Technol 54, 3148-3158.
- FOCUS, 2014. Generic guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration (Version: 1.1, 18 December 2014).
- Formacare, 2021. Pilot project report on the grouping of Formacare Amino Polymers. unpublished.
- Gladfelter, A.S., James, T.Y., Amend, A.S., 2019. Marine fungi. Current biology : CB 29, R191-R195.
- Gómez, E.F., Michel, F.C., 2013. Biodegradability of conventional and bio-based plastics and natural fiber composites during composting, anaerobic digestion and long-term soil incubation. Polymer Degradation and Stability 98, 2583-2591.
- Government of Canada, 2021. Guidance Document for the Notification and Testing of New Chemicals and Polymers. draft.

- Haider, T.P., Volker, C., Kramm, J., Landfester, K., Wurm, F.R., 2019. *Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society*. *Angewandte Chemie-International Edition* 58, 50-62.
- Hashimoto, K., Sudo, M., Ohta, K., Sugimura, T., Yamada, H., Aoki, T., 2002. Biodegradation of nylon4 and its blend with nylon6. *Journal of Applied Polymer Science* 86, 2307-2311.
- ISO, 2011. ISO 10640 - *Plastics — Methodology for assessing polymer photoageing by FTIR and UV/visible spectroscopy*.
- ISO, 2012. ISO 10210 - *Plastics – Methods for the preparation of samples for biodegradation testing of plastic materials*.
- ISO, 2013. ISO 472 - *Plastics – Vocabulary (ISO 472:2013)*; Trilingual version EN ISO 472:2013. DIN EN ISO.
- ISO, 2016a. ISO 18830 - *Plastics — Determination of aerobic biodegradation of non-floating plastic materials in a seawater/ sandy sediment interface — Method by measuring the oxygen demand in closed respirometer*.
- ISO, 2016b. ISO/TS 19022 - *Plastics — Method of controlled acceleration of laboratory weathering by increased irradiance*.
- ISO, 2017. ISO 4582 - *Plastics — Determination of changes in colour and variations in properties after exposure to glass-filtered solar radiation, natural weathering or laboratory radiation sources*.
- ISO, 2018a. ISO 10634 - *Water quality — Preparation and treatment of poorly water-soluble organic compounds for the subsequent evaluation of their biodegradability in an aqueous medium*.
- ISO, 2018b. ISO 14852 - *Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of evolved carbon dioxide*.
- ISO, 2019a. ISO 14851 - *Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by measuring the oxygen demand in a closed respirometer*.
- ISO, 2019b. 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 (ISO 17556:2019)*;
- ISO, 2019c. ISO 22404 - *Plastics — Determination of the aerobic biodegradation of nonfloating materials exposed to marine sediment — Method by analysis of evolved carbon dioxide*.
- ISO, 2020a. ISO 19679 - *Plastics — Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sediment interface — Method by analysis of evolved carbon dioxide*.
- ISO, 2020b. ISO 22403 - *Plastics — Assessment of the intrinsic biodegradability of materials exposed to marine inocula under mesophilic aerobic laboratory conditions — Test methods and requirements*.
- ISO, 2020c. ISO 22766 - *Plastics — Determination of the degree of disintegration of plastic materials in marine habitats under real field conditions*.
- ISO, 2020d. ISO 23977-1 - *Plastics — Determination of the aerobic biodegradation of plastic materials exposed to seawater — Part 1: Method by analysis of evolved carbon dioxide*.
- ISO, 2020e. ISO 23977-2 - *Plastics — Determination of the aerobic biodegradation of plastic materials exposed to seawater — Part 2: Method by measuring the oxygen demand in closed respirometer*.
- ISO, 2021a. ISO 5148 - *Plastics — Determination of specific aerobic biodegradation rate of solid plastic materials and disappearance time (DT50) under mesophilic laboratory test conditions*.
- ISO, 2021b. ISO 23517 - *Plastics — Soil biodegradable materials for mulch films for use in agriculture and horticulture — Requirements and test methods regarding biodegradation, ecotoxicity and control of constituents*.
- ISO, 2021c. ISO 23832 - *Plastics — Test methods for determination of degradation rate and disintegration degree of plastic materials exposed to marine environmental matrices under laboratory conditions*.
- Junker, T., Coors, A., Schuurmann, G., 2019. *Compartment-Specific Screening Tools for Persistence: Potential Role and Application in the Regulatory Context*. *Integr Environ Assess Manag* 15, 470-481.

- Kang, B.R., Kim, S.B., Song, H.A., Lee, T.K., 2019. Accelerating the Biodegradation of High-Density Polyethylene (HDPE) Using *Bjerkandera adusta* TBB-03 and Lignocellulose Substrates. *Microorganisms* 7, 304.
- KBBPPS, 2015. Biodegradability-standards-assessment-report. <https://www.biobasedeconomy.eu/projects/kbbpps-knowledge-based-bio-based-products-pre-standardization/>.
- Kjeldsen, A., Price, M., Lilley, C., Guzniczak, E., Archer, I., 2019. A Review of Standards for Biodegradable Plastics. Industrial Biotechnology Innovation Centre, p. 33p.
- Kögel-Knabner, I., 2002. The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology and Biochemistry* 34, 139-162.
- Lehmann, M., Oehlschlägel, L.M., Häusl, F.P., Held, A., Gekle, S., 2021. Ejection of marine microplastics by raindrops: a computational and experimental study. *Microplastics and Nanoplastics* 1.
- McDonough, K., Itrich, N., Casteel, K., Menzies, J., Williams, T., Krivos, K., Price, J., 2017. Assessing the biodegradability of microparticles disposed down the drain. *Chemosphere* 175, 452-458.
- Meereboer, K.W., Misra, M., Mohanty, A.K., 2020. Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites. *Green Chemistry* 22, 5519-5558.
- Nelson, T.F., Remke, S.C., Kohler, H.-P.E., McNeill, K., Sander, M., 2020. Quantification of Synthetic Polyesters from Biodegradable Mulch Films in Soils. *Environ Sci Technol* 54, 266-275.
- OECD, 1992. Test No. 301: Ready Biodegradability. OECD Publishing.
- OECD, 2006. OECD GUIDELINES FOR THE TESTING OF CHEMICALS - REVISED INTRODUCTION TO THE OECD GUIDELINES FOR TESTING OF CHEMICALS, SECTION 3.
- OECD, 2009. DATA ANALYSIS OF THE IDENTIFICATION OF CORRELATIONS BETWEEN POLYMER CHARACTERISTICS AND POTENTIAL FOR HEALTH OR ECOTOXICOLOGICAL CONCERN.
- OECD, 2019. Guiding Principles and Key Elements for Establishing a Weight of Evidence for Chemical Assessment. Series on Testing and Assessment No 311.
- Open-Bio, 2016. WP5: in-situ biodegradation. <https://www.biobasedeconomy.eu/projects/open-bio/>.
- Ott, A., Martin, T., Whale, G., Snape, J., 2019. Improving the biodegradability in seawater test (OECD 306).
- Ott, A., Martin, T.J., Acharya, K., Lyon, D.Y., Robinson, N., Rowles, B., Snape, J.R., Still, I., Whale, G.F., Albright, V.C., Bäverbäck, P., Best, N., Commander, R., Eickhoff, C., Finn, S., Hidding, B., Maischak, H., Sowders, K.A., Taruki, M., Walton, H.E., Wennberg, A.C., Davenport, R.J., 2020. Multi-laboratory Validation of a New Marine Biodegradation Screening Test for Chemical Persistence Assessment. *Environ Sci Technol* 54, 4210-4220.
- Park, B.-D., Jeong, H.-W., 2011. Hydrolytic stability and crystallinity of cured urea-formaldehyde resin adhesives with different formaldehyde/urea mole ratios. *International Journal of Adhesion and Adhesives* 31, 524-529.
- Pischedda, A., Tosin, M., Degli-Innocenti, F., 2019. Biodegradation of plastics in soil: The effect of temperature. *Polymer Degradation and Stability* 170.
- Polman, E.M.N., Gruter, G.M., Parsons, J.R., Tietema, A., 2020. Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: A review. *Sci Total Environ* 753, 141953.
- Redman, A.D., Bietz, J., Davis, J.W., Lyon, D., Maloney, E., Ott, A., Otte, J.C., Palais, F., Parsons, J.R., Wang, N., 2021. Moving persistence assessments into the 21(st) Century: A role for weight-of-evidence (WoE) and overall persistence (Pov). *Integr Environ Assess Manag*.
- Ruggiero, F., Gori, R., Lubello, C., 2019. Methodologies to assess biodegradation of bioplastics during aerobic composting and anaerobic digestion: A review. *Waste Manag Res* 37, 959-975.
- Sánchez, C., 2020. Fungal potential for the degradation of petroleum-based polymers: An overview of macro- and microplastics biodegradation. *Biotechnol Adv* 40, 107501.

- Sander, M., 2019. Biodegradation of Polymeric Mulch Films in Agricultural Soils: Concepts, Knowledge Gaps, and Future Research Directions. *Environmental Science and Technology* 53, 2304-2315.
- SAPEA, 2020. BIODEGRADABILITY OF PLASTICS IN THE OPEN ENVIRONMENT.
- Sommer, F., Dietze, V., Baum, A., Sauer, J., Gilge, S., Maschowski, C., Gieré, R., 2018. Tire Abrasion as a Major Source of Microplastics in the Environment. *Aerosol and Air Quality Research* 18, 2014-2028.
- Su, S., Kopitzky, R., Tolga, S., Kabasci, S., 2019. Polylactide (PLA) and Its Blends with Poly(butylene succinate) (PBS): A Brief Review. *Polymers (Basel)* 11.
- Tosin, M., Pischedda, A., Degli-Innocenti, F., 2019. Biodegradation kinetics in soil of a multi-constituent biodegradable plastic. *Polymer Degradation and Stability* 166, 213-218.
- Tosin, M., Weber, M., Siotto, M., Lott, C., Degli Innocenti, F., 2012. Laboratory test methods to determine the degradation of plastics in marine environmental conditions. *Front Microbiol* 3, 225.
- Trainic, M., Flores, J.M., Pinkas, I., Pedrotti, M.L., Lombard, F., Bourdin, G., Gorsky, G., Boss, E., Rudich, Y., Vardi, A., Koren, I., 2020. Airborne microplastic particles detected in the remote marine atmosphere. *Communications Earth & Environment* 1.
- Trapp, S., Brock, A.L., Nowak, K., Kastner, M., 2018. Prediction of the Formation of Biogenic Nonextractable Residues during Degradation of Environmental Chemicals from Biomass Yields. *Environ Sci Technol* 52, 663-672.
- Wood, 2020. Scientific and technical support for the development of criteria to identify and group polymers for Registration/ Evaluation under REACH and their impact assessment.
- Zumstein, M.T., Narayan, R., Kohler, H.P.E., McNeill, K., Sander, M., 2019. Dos and Do Nots When Assessing the Biodegradation of Plastics. *Environ Sci Technol* 53, 9967-9969.
- Zumstein, M.T., Schintlmeister, A., Nelson, T.F., Baumgartner, R., Woebken, D., Wagner, M., Kohler, H.P.E., McNeill, K., Sander, M., 2018. Biodegradation of synthetic polymers in soils: Tracking carbon into CO₂ and microbial biomass. *Science Advances* 4, eaas9024.