What can we learn from biodegradation of natural polymers for regulation?

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Abstract

Synthetic polymers are chemicals of emerging concern for the environment, which is mainly attributed to their persistence in environmental compartments. On the other hand, polymers exist in nature as well. They are regarded of no concern for the environment. The present article focusses on the environmental fate of natural polymers and the implications on the persistence assessment for synthetic polymers. Natural polymers vary widely in structure, function, and properties. Crystallinity, wettability and surface area are important influencing factors on the (bio) degradation kinetics. Chemical and enzymatic hydrolysis is the most important process for the degradation of natural polymers, which for particulate material takes place either by bulk or surface erosion. Some natural polymers are degraded rapidly, but in other cases, degradation of natural polymers takes very long until complete mineralization. These differences in biodegradability are a result of evolution as they have to fulfil specific functions in nature which might require a certain persistency. Consequently, many natural polymers would have to be considered persistent or very persistent (P or vP) based on the available studies using the standard assessment approach. At the same time, they are considered no concern to the environment for good reasons. The analysis emphasizes that mineralization alone is not a resilient persistence endpoint for polymers. This needs to be recognized when assessing synthetic polymers, many of which would fulfil the existing P/vP criteria as well. For such synthetic polymers, it would be important to establish meaningful endpoints and polymer specific criteria to enable an adequate persistence assessment using a weight-of-evidence approach.

Keywords Natural polymers, Occurrence and fate, Biodegradation processes, Persistence assessment

Background

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*" [1, 2]. In the future, synthetic polymers will most likely require registration under REACh, and thus environmental hazard and fate assessment as well as persistence assessment need to be included.

The term polymer can encompass a very diverse range of chemicals which needs to be defined more precisely. Using the REACh polymer definition [1], polymers comprise such diverse substances as insoluble solid 'plastic' polymers, liquid polymers, soluble polymers, smaller oligomeric polymers (e.g., surfactants), etc. In addition, we must differentiate between polymeric substances and plastic materials or articles/products. A polymer as a substance is a mixture of multiple components, where the components are very similar (macro) molecules with, for example, different chain lengths. There are four basic polymer structures (and probably many variations of these): linear, branched, crosslinked, and networked polymers. Typically, polymers are < 1 Mio Daltons (Da), but higher molecular weights are also possible.

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In recent years, polymers and especially microplastic are of emerging concern for the environment. This concern is mainly attributed to their persistence and occurrence in environmental compartments. In general, the nature of polymers being multi-constituent substances, or even UVCBs, i.e., substances which are of unknown or variable composition, complex reaction products or of biological materials, makes quantification extremely challenging. Relatively few examples exist of the quantification of specific polymers in environmental media, either in the laboratory or the field [3]. Destructive and non-destructive techniques are applied to identify the composition of the polymers [4]. Common destructive technique is pyrolysis gas chromatography–mass spectrometry (Pyr-GC/MS), and Fourier-transform infrared spectroscopy (FTIR) is mostly used as non-destructive technique. With regard to FTIR, Roscher et al. [5] emphasize the importance of including valid natural materials within polymer reference databases used in MP analyses. This is in order to improve data quality and avoid false-positive assignments due to matrix effects.

Microplastics (MP) have been found in the environment in varying concentrations by several monitoring studies. However, the numbers published have to be considered with care because a recent interlaboratory study with more than 100 laboratories organised by the Joint Research Centre (JRC) [6] indicated a very high variability in the quantification of MP from aqueous samples by different laboratories. Results obtained in the study of an artificial reference sample do not even show a common trend, which questions the general reliability of current MP analytical methods. Moreover, natural polymers may influence the analysis of MP [5]. Recent reviews about occurrence of nanoplastic (NP) in the environment [7–9] indicate that sampling and characterization of NP in the environment is even more challenging. Unified protocols for sampling and measurement are missing, and thus some studies found NP, others not.

Since 2017, the German environment agency has conducted several research projects to establish, validate and standardise analytical techniques for synthetic MP in soils and other environmental matrices [10]. Techniques developed are currently used to determine actual background concentrations of synthetic MP in soils.

Certain existing frameworks for safety assessment question 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 [11]. Many of the identified knowledge gaps relate to the applicability of standard analytical tools, test methods and in silico models [3]. Four major challenges have been identified for assessing and interpretation of polymer biodegradation and persistency [12]: (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.

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 developed for well-defined low molecular weight (LMW) substances, that are typically mono-constituent and water soluble [3]. Polymers usually do not fit the scope of these guidelines. For this reason, the assessment of the environmental fate properties of polymers is associated with considerable challenges that go beyond the assessment of LMW substances. Several specific standard protocols have been adapted or developed for (bio) degradability testing of plastic materials. These specific standards have already been reviewed in several reports and articles [3, 13–18]. The available standards are mainly ISO or ASTM guidelines, which are often very similar. Due to the lack of appropriate analytical methods, the degradation endpoint in these standard methods is mineralization (O_2 consumption or CO_2 evolution), and the mineralization of a (natural) reference material, mostly cellulose, serves as the validation criteria.

Polymers are formed in nature as well, which comprise for example polysaccharides such as cellulose or starch, proteins such as collagen or gelatine [19, 20] or lignin. In nature the polymers have different functions, e.g., storage materials, cell walls, protection against microbial attack (plants) or exoskeleton (insects) and the polymers have, through evolution, been optimised to fulfil these functions. Without these natural polymers and their specific properties, life as we know it, is not possible.

There is no evidence that natural polymers are of concern for the environment, but there is evidence that they could become, e.g., beneficial components to the soil. What does the fact that they don't raise any environmental concern, tell us about the persistence assessment of synthetic polymers?

Methodology

The present article is based on the final reports from ECO 52 [21, 22], but is basically limited to information on natural polymers with a focus on behaviour of particulate materials and not on water soluble materials. This information is used to discuss how to advance the persistence assessment of synthetic polymers.

Within the ECO 52 project a literature search has already been conducted between April 2020 and December 2020 in Pubmed, WebOfScience and Scopus (search terms: (bio)degradation or persistence in combination with polymer or plastic) as well as in the Web using

Google. This search has been limited to reviews published in the last 5 years, which resulted in about 5000 hits. From this search about 1000 papers have been selected which contain the word biodegradation in title, or information about polymer biodegradation, persistence, or weathering. Afterwards, these reviews supplemented with articles from the search of the last 2 years have been screened for relevance by reviewing the title and abstract. In total, this search strategy resulted in more than 100 relevant documents which have been evaluated in depth.

Recently, this search has been supplemented by an updated literature search between September 2022 and December 2022 specifically for reviews on biodegradation of natural polymers. With the search query on biodegradation AND natural polymer AND review about 1000 references could be found in Pubmed published in the last two years (Fig. 1). Of these about 50 references have been identified, again by reviewing title and abstracts, as more or less relevant and subsequently evaluated in-depth. Additional references were evaluated which were identified as relevant in the evaluated reviews (secondary citations), and which were identified by google and google scholar within a search on specific natural polymers, such as natural rubber.

Results and discussion
Types of natural polymers
Polymers exist in nature as well, and contribute to different essential functions for living organisms. These so-called natural polymers include natural rubber, cellulose, hemicellulose, starch, lignin, chitin, cutin; sometimes they 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 [21]. In the literature, proteins are often assigned to natural polymers as well [19, 20]. Natural polymers may be built by one monomer unit such as glucose in cellulose or starch, whereas others such as hemicellulose or lignin are built by different monomer units. In natural materials (e.g. straw wheat straw, spruce, and birch, etc.) the contents of different polymers can vary significantly [23].

Some examples of natural polymers and their source and structural and/or morphological descriptors are given in Table 1 (not exhaustive). Exemplarily the structures of cellulose and lignin are given in Fig. 2.

Overall, natural polymers could have different structural linkages and a high range of molecular weights [21]. Often, they are polysaccharides or their derivatives with weak α-glycosidic bonds or stronger β-glycosidic linkages. Natural polymers could be crystalline, semi-crystalline or amorphous, are often insoluble, and could

be hydrophilic but also hydrophobic. Thus, different structural and morphological descriptors and physicochemical properties can be assigned to natural polymers. Based on these descriptors and properties, some natural polymers are expected to be hydrolytically more stable than others, and it is obvious that as a consequence they will have different potential for (bio)degradation [21]. For optimal functions, materials in nature are usually mixtures of different natural polymers, which further increases the complexity.

Occurrence of natural polymers in the environment
Natural polymers are part of the environment, e.g. starch is produced for energy storage, chitin is part of the insect exoskeleton, and cellulose, lignin, cutin are part of cell walls or plant cuticles, etc. For this reason, in the environment these natural polymers and/or their transformation products will often be found in the top layer of soil. The type and degree of natural polymers in the environment depends on the vegetation, and degradation potential and is related to the nature of vegetation, climate, and land-use as well. Plant derived polymers also form the basis for natural soil organic matter (SOM) [25]. In fact, the processes of biodegradation and SOM generation are connected. Mostly, parts of less degradable natural polymers are selectively incorporated into humic substances [41]. The absolute amount of soil organic matter is a result of the equilibrium between incorporation into the soil and the degradation processes. Adapted microorganisms, i.e., bacteria and fungi, will be found depending on the sources of energy, the climate and soil characteristics.

Natural polymers are found in the aquatic environment as well. This could be the result of the aquatic vegetation or as a run-off from the soil compartment. Primpke et al. [42] stated that in total over 50% of all fibres found in wastewater treatment plant (WWTP) samples were of natural origin, 11% of inorganic and 39% of a synthetic nature. Furthermore, cellulose based fibres contributed to more than 50%. Moreover, plant cuticles can influence the identification and quantification of microplastic (MP) concentrations [5].

Fate of natural polymers in the environment
Distribution
As mentioned above, in the environment natural polymers and/or their transformation products will be mostly found in the top layer of soil, where plant derived polymers form the basis for natural soil organic matter. At least water insoluble soil organic matter, which is a sink for natural polymers, does not move vertically in soils significantly, as soil organic matter is usually located in the upper soil horizons. Active transport into deeper soil

Table 1 Examples of natural polymers and their structural and morphological descriptors

| Natural polymer	Source	Structure	Morphology	Properties	References
Starch	Produced by most green plants for energy storage, and (major) ingredient in wheat, potatoes, maize (corn), and rice, banana peels	Polysaccharide; branched amylopectin and linear amylose chains; Weak α-glycosidic bonds	Granular shape, alternating amorphous and semi crystalline layers	White, tasteless and odourless powder; mostly insoluble in cold water or alcohol	Polman et al. [24], Kögel-Knabner [25]
Cellulose	Plant cell walls rice hulls cotton	Polysaccharide $(C_6H_{10}O_5)_n$; D-glucose units; stronger β-glycosidic linkages; linear (unbranched) chain with degree of polymerization (DP) values of several hundred to many thousand depending on the origin and treatment	Crystalline (but small fraction amorphous)	Tasteless and odourless; hydrophilic; insoluble in water and most organic solvents	Polman et al. [24], Klemm et al. [26], Kulkarni et al. [27]
Hemicellulose	Plant cell walls	Heterogeneous group of polysaccharides; pentosen (xylose, arabinose) and hexosen (glucose, mannose, galactose), and can contain acidic forms, β-(1,4)-linked backbones; branched consists of shorter chains—500–3,000 sugar units	Random, amorphous structure with little strength	Water solubility depends on type and degree of substitution	Kulkarni et al. [27], Scheller and Ulvskov [28], Ebringerová et al. [29]
Pectin	Plant cell walls citrus peels apple pomace banana peels	Linear polysaccharide, galacturonic acid interrupted with L-rhamnose units, α-glycosidic bonds few hundred to about one thousand units per molecule,	Gelling depending on type and structure	Hydrophilic; soluble in water, gel in aqueous solution if dissolved at higher temperature	Kulkarni et al. [27], BeMiller [30], Acquavia et al. [31]
Lignin	Plant cell walls wood and bark	Consists of the aromatic coniferyl, coumaryl and sinapyl alcohols, bound together by C—O—C or C—C linkages; about 50% of these are the β-O-4 aryl ether type	Amorphic three-dimensional polymer	Insoluble lacks in hydrolyzable linkages	Polman et al. [24], Datta et al. [32], Zhang et al. [23], Tyagi et al. [33]
Cutin	Plant cuticle tomato waste	Polyester polymer consisting of omega hydroxy acids and their derivatives composed of various characteristic long-chain (C16 and C18) alkanoic acids (most of them saturated) substituted by hydroxy, carbonyl, and epoxy groups	Lipid, waxy polymer amorphous and flexible three-dimensional	Insoluble in organic solvents; water resistant (hydrophobic, lipophilic)	Riederer and Schonherr [34], Briggs [35], Acquavia et al. [31]
Natural rubber	Elastomer made from latex, a sticky, milky plant sap	Cis-1,4-polyisoprene; allylic C–H bonds in each repeat unit	Strain crystallization	Insoluble in water	Rose and Steinbüchel [36], Greve [37], Konno [38], Shah et al. [39]
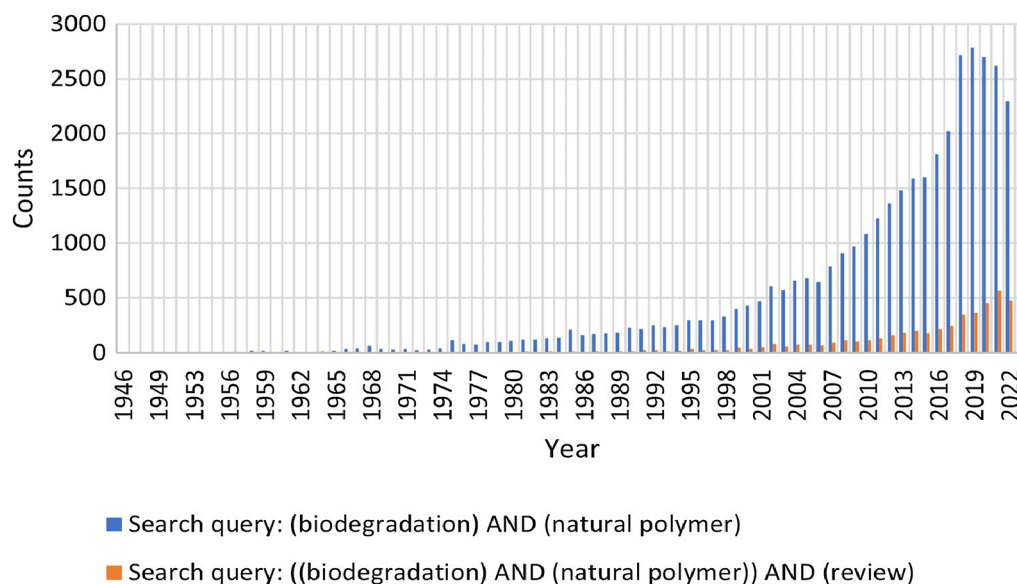
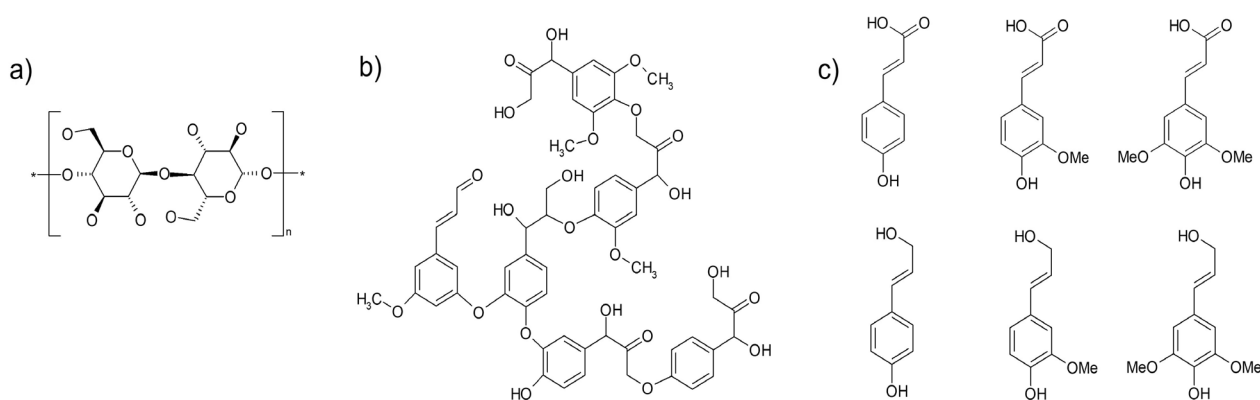**Fig. 1** Results of the literature search in Pubmed

Fig. 2 Structures of typical natural polymers **a** Cellulose, **b** Lignin, **c** Building units of Lignin (adapted from [23, 25, 40])

layers is usually carried out by soil organisms or vertical burrows (e.g., earthworm burrows).

Natural polymers in the aquatic environment (e.g., sceleton or fiber materials from macrophytes) are floating or deposited as organic matter into the sediment and transported by natural sediment transport [43, 44].

Degradation processes

Biodegradation of natural polymers is a stepwise process and the slowest of the processes determines the overall mineralization rate, which is the current indicator for (bio)degradation of polymers. The process of polymer (bio)degradation can be divided into four steps [33, 45, 46]:

a. Biodeterioration
b. Depolymerization
c. Bioassimilation, and/or
d. Mineralization

Thereby, microbial biofilms on the polymeric material results in superficial degradation and the formation of smaller fragments. Microbial enzymes then in turn catalyse the depolymerization of the polymer chain into oligomers, dimers, or monomers. These smaller molecules can be taken up into microbial cells and degraded further [47].

The structural and morphological properties as well as several processes are important for the fragmentation of the polymeric material, and thus are influencing

the different (bio)degradation kinetics. Larger fragments can be incorporated into the humus matrix which stabilizes them against further degradation.

Key processes associated with organic matter cycling in soils are litter deposition, transformation, decomposition, mineralization, humification, partitioning, assimilation and stabilization [41]. Thereby, decomposition is the breakdown of organic macromolecules into smaller organic molecules and inorganic constituents of organic matter [41]. This process is usually mediated by micro-organisms and includes depolymerization and oxidation reactions [41]. Mineralization is defined as the conversion into the inorganic constituents of the organic matter [41], and results under aerobic conditions in the final products carbon dioxide and water. However, natural polymers must not be degraded to carbon dioxide, the organic carbon can be converted in humic substances or assimilated into the biomass. Plant particulate material forms the basis for humification. Humic substances are very stable, radiocarbon dating put the carbon turnover in soil organic matter in the range of hundreds to thousands of years. The deeper the soil layers, the older the organic substances found [48]. According to Oades [49], humification has to be assessed as prolonged stabilisation of organic substances against biodegradation.

It is expected that sunlight will contribute to degradation and depolymerization processes of natural polymers [50–52]. In addition, structures of the natural polymers are often hydrolytically unstable, e.g., esters. For this reason, the most important process for degradation of natural polymers is the hydrolysis of ester bonds [24]. Hydrolysis can be divided into chemical and enzymatic hydrolysis. In the latter case, hydrolysis is promoted by specific enzymes, so that the microorganism (including fungi) can use the polymers as an energy source or for its biomass.

This enzymatic degradation, especially by fungal enzymes, plays a major role in the (bio)degradation of natural polymers. For example, cellulose and starch are enzymatically hydrolysed to glucose by extracellular enzymes [53]. The group of enzymes most responsible for extracellular cellulose degradation are cellulases, which will break the β-glycosidic links [54], and α/β-amylases as well as oxidoreductases [53]. Starch is degraded by glycoside hydrolases, such as α-amylase, β-amylase, glucoamylase and α-glucosidase, which are all specialised in hydrolysing α-glycosidic bonds [24, 54]. In addition, starch can be made more susceptible to biodegradation by gelatinisation [24]. Fungi and eubacteria form the largest share of the cellulolytic (cellulose-degrading) microorganisms as well [24, 25]. For the degradation of lignin many organisms and enzymes are involved, which
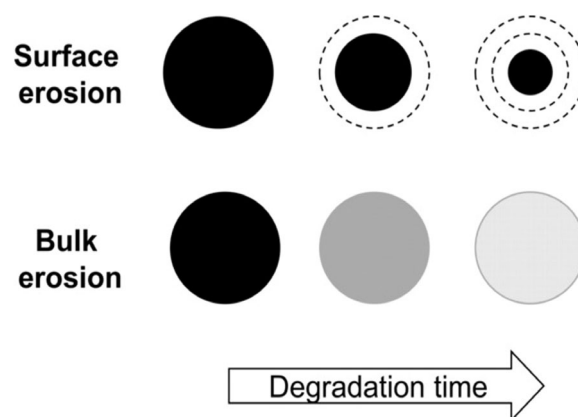

Fig. 3 Surface and bulk erosion (taken from [45])

Fig. 4 Picture of snag illustrating different degradation phases (photo by D. Hennecke)

reflects the complexity of lignin molecules [24], and thus, it is obvious that the biodegradation rate is slower.

Another influencing factor is, that natural polymers are often form particulate material. Hydrolysis of particulate material proceeds either by bulk or surface erosion (Fig. 3). Bulk erosion describes degradation that occurs uniformly through the thickness of a polymeric item, and surface erosion describes a decrease in the surface

thickness [45]. Which process dominates depends on if the material is amorphic, or (semi) crystalline. Enzymes preferentially attack the amorphous parts [46], and thus amorphous or less-ordered regions degrade more easily than crystalline regions [47]. Moreover, as enzymes are relatively large and are unable to permeate the structure of polymers, in comparison to smaller chemicals or free radicals [55, 56], the biotic (enzymatic) degradation is often limited to the polymer surface. In addition, it is expected that stepwise degradation of chain length occurs for high molecular weight molecules.

In summary, several further processes have an impact on degradation kinetics of natural polymers. Consequently, not all carbon of the polymer material can be attacked by microorganisms simultaneously, leading to a stepwise degradation where the slowest step determines the degradation rate. All natural polymers which are hydrolytically more stable need additional factors (e.g., specific enzymes) to be degraded in a reasonable timescale. If other better energy sources are available for degraders (easily degradable substances), the biodegradation of the natural polymer slows down. This, together with the above mentioned structural and morphological properties such as crystallinity and wettability, in turn will result in different (bio)degradation kinetics under different conditions.

Degradation data

The (bio)degradation of naturally occurring polymers especially in soils has long been a research interest since soil organic matter is important for most soil functions like sorption capacity, water retention, nutrient cycling, and biological activity. Degradation data of substances in soil is usually obtained performing standard tests, e.g., according to OECD testing guidelines. However, results from OECD testing guidelines (screening and simulation studies) with natural polymers are available in rare cases only. If any data on (bio)degradation of natural polymers are available, the tests follow ISO or ASTM standards (mineralization) or are non-guideline studies. The latter studies often only provide results on mass loss, or loss of functionality (indication for degradation). As cellulose (microcrystalline powder or as ashless filter material) is the reference material for ISO or ASTM test systems, plenty of data are available for cellulose.

Data for some natural polymers have been compiled in reviews on so called "bioplastics". For example, an overview about degradation pathways and available data for starch, cellulose, lignin and modified natural polymers has been published by Polman et al. [24]. The review by Kögel-Knabner [25] provides information that helps to identify the changes occurring during biodegradation of plant litter in soils, and contains a table with information on biodegradability (percentage mineralization at different time points up to 28 weeks) of several natural polymers in soil. However, detailed information on the test method are missing. A review of the fate of lignin in soil is presented by Thevenot et al. [57].

The available generic information about degradation of selected natural polymers is summarized in Table 2.

In addition, some data on (bio)degradation potential are available for natural materials and products [25, 59, 79]. In this context it is important that, as already mentioned above, natural materials are often mixtures of polymers and monomer units, and rarely pure polymeric materials.

McDonough et al. [79] investigated the degradation potential of natural materials (stearyl stearate, jojoba wax, bees wax, rice bran wax, blueberry seeds, walnut shells) using a (modified) OECD 301 B test system. The natural materials were applied as microparticles, milled, or as powder. The organic carbon content and the particle size of the different materials have been specified. Some of the natural materials show significantly different degradation kinetics than others. Although the particle size of blueberry seed was larger (100% > 500 μm), the material shows a higher degradation potential than walnut shells with the main particle fraction between 250 and 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 [59]. Although the guideline was in the meantime revised (ASTM 5998–18), and the test may be regarded as invalid due to not complying with the minimum biodegradation of the reference material given in the revised version, some interesting conclusions can be drawn. 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 and 40%, which was reached relatively quickly (< 100 days). This indicates that the slow degrading material contains some (polymeric) constituents which are hardly mineralized.

The review by Kögel-Knabner [25] presents, for natural materials, mineralization data (CO_2 evolved) in soil at different time points up to 28 weeks. Although it seems that it is a screening test, the kinetics verify that starch takes longer to biodegrade than glucose. In general, most proteins and polysaccharides are rapidly utilized but at a slightly slower rate than readily available small-molecular-weight substrates (or monomer units) such as sugars, amino acids, and aliphatic acids. These are metabolized

within a few hours or days [58]. Whereas natural substances such as glycine, glucose, cellulose, or starch resulted in high mineralization (> 80%), other natural materials such as walnut wood, almond shells, pine needles resulted in significant lower biodegradation potential (< 60%). Wheat straw shows a mineralization of about 67%, which confirms the lower potential of lignin in comparison to cellulose. Only 50–60% of the total organic matter of plant litter is accounted for by chemical degradation techniques [58].

Cellulose is also the main component of paper or paperboard. Today, paper contains usually synthetic polymers as additives [80], thus paper or paperboard cannot seriously be considered as a pure natural material. Nevertheless, some degradation data are available. The data demonstrates that corrugated board is a biodegradable and compostable material [81]. Pagga et al. [82] observed about 80% mineralization of paper in about 30 days in a laboratory controlled composting test, whereas Sridach et al. [83] found a weight loss of up to 70% in 7 weeks for uncoated board.

In summary, the available data about biodegradability of natural polymers vary. Available studies are often on composting or field studies in soil, and thus are not conducted according to standardized test guidelines. Information about all compartments (soil, aqueous, marine, sediment) for the same polymer are hardly available, particularly information on degradation in sediment are mostly lacking. As an endpoint mineralization has often been measured, but also other endpoints such as mass loss were reported.

Nevertheless, natural polymers are generally expected to be biodegradable. However, the available data indicate that the rates could be highly variable depending on the structural and morphological properties of the polymers and the conditions such as temperature, humidity, availability of oxygen, presence of competent degraders/decomposer groups, etc. In particular, skeleton polymers or polymers that protect organisms against microbial attacks do not degrade easily—that is one of the essential key properties of these materials.

Natural materials and products, e.g., rice hull, coconut coir, wheat straw, walnut shells, etc., have been tested in different test systems as well. In most cases these are less degradable in the test systems used in comparison to cellulose or starch with regard to mineralization. Often slow degrading material contains some constituents which are hardly mineralized. Instead, it is incorporated into SOM.

Consequences for persistence assessment of synthetic polymers

Like natural polymers, synthetic polymers are a class of substances which in products are often designed, to be stable during a relatively long use phase as much as possible to fulfil performance requirements.

A better understanding of the fate of natural polymers, considering similarities and differences between natural and synthetic polymers, gives an insight into which processes may be relevant and important for an appropriate persistence assessment of synthetic polymers. Moreover, it gives an input into the decision on the relevance of persistence and potentially provides benchmarks for the (hazard) assessment of polymers. For the comparison of natural and synthetic polymers, preference should be given to literature which compares the degradation potential of different polymer sources using the same method.

Both natural and synthetic polymers are formed by polymerization of small molecules. Although building units of different natural polymers are sometimes similar, natural polymers, vary in structure, function, and properties. These properties are attributed to the polymer's molecular size as well as 2D and 3D structure (linear, branched, crosslinked, and networked polymers). This also has consequences for their biodegradation behaviour. If natural polymers will be synthesized in the laboratory, the same biodegradability would be expected as the equivalent naturally formed polymer. In this special case biodegradability is not a question of natural or synthetic "manufacturing". However, natural materials do not consist of one pure polymer substance but are mostly a combination of different polymers and further substances, that cannot yet be produced synthetically.

In the literature, there is only a limited number of degradation study results available for natural polymers, which are based often on weight loss only (Table 2). More data are available for synthetic polymers. Several compilations of available degradation data for synthetic polymers have been presented in recent reviews such as Kjeldsen et al. [14] based on data compilation from Emadian et al. [84], and Burgstaller et al. [85] cited in an EPA network report [86]. Some further degradation data are available from primary literature sources as well, which are partly cited in these reviews, e.g., Meereboer et al. [55], Gómez and Michel [59], Hashimoto et al. [87], Arcos-Hernandez et al. [88] etc.. Further relevant literature using standardized methods in soil are available from Novamont [60–63] and EU projects KBBPPS [89] and Open-Bio [90]. Data for water soluble polymers such as PEGs and some blends are available from Bernhard et al. [91], Eubeler et al. [92], Duis et al. [93]. Water soluble, poorly soluble, and water insoluble/particulate polymers show quite different fate behaviour [3]. In addition, Hennecke et al. [94] presented a lysimeter study of cationic polyacrylamide copolymers (PAMs) using radiolabelled synthetic polymer and thus mass balance was

possible. This study shows that there was practically no vertical movement of polymer despite the proven significant reduction of the polymer backbone chain length over two years.

Information from degradation tests for synthetic polymers can be summarized as follows [21, 22]:

– Metrics used for available (bio)degradation data (laboratory as well as mesocosm/field tests): respirometry, mass loss or specific surface degradation rate (SSDR), tensile test.
– Fragmentation by weathering; hydrolysis relevant (e.g., for esters) but also additional processes such as deacetylation
– Enzymes play a major role
– Standard methods on biodegradation of polymers are usually based on mineralization only
– Limited number of studies according to ISO methods available (mainly for so called "biodegradable" synthetic polymers); limited data for soil or water, very limited data for sediment
– Results for blends can overestimate the biodegradation potential if selected constituents are not biodegradable
– Data with simulation studies are rare

The overview indicates that one reason for the limited number of reliable studies is the challenge to follow the degradation of polymers, independent if they are natural or synthetic polymers. The lack of polymer specific degradation endpoints and at the same time very limited and complex chemical analysis makes it difficult to set up appropriate studies. Moreover, the specific physico-chemical properties of polymers result in specific technical limitations for the applicability of existing standard guidelines. Therefore, mineralization and gravimetric mass loss often serve as the degradation endpoints, simply because they can be measured with reasonable effort. Following biodegradation by mineralization, i.e., using indirect parameters such as O_2 consumption or CO_2 evolution as in the screening test systems of OECD testing guidelines or the polymer-specific ISO standards, also has some limitations. This screening is often not suitable for blends, as it is unclear if all components degrade at the same rate. More than likely, they do not. In addition, polymers typically consist of large molecules, which are mostly solid and insoluble in water. In fact, the currently proposed MP restriction excludes water soluble synthetic polymers, which means that most polymers to be tested will be non-water soluble. The limited bioavailability of those large molecules can be already the reason for failing the test. However, since this is a typical property of polymers, the suitability of an aquatic degradation test

must be critically questioned. Test challenges can be summarized as follows [22]:

• 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

Based on these deficiencies, the available results from screening test systems following the OECD 301 series should be interpreted carefully. It might be that they have a systemic limitation, and evidence for reliability is needed.

Moreover, these test systems commonly use an inoculum from the targeted environment (e.g., from wastewater treatment plant (WWTP), from WWTP effluent or aqueous soil extracts). During pre-treatment the amount of natural organic load is decreased, so that the blank respiration is reduced to an acceptable level within the biodegradation experiment. However, such treatments are likely to remove most or all extracellular enzymes from the inoculum, so that degradation testing of substances and materials that require breakdown by extracellular enzymes may result in artificially low biodegradation rates [95]. As mentioned above, these extracellular enzymes are important for polymeric materials. However, highly active test matrices are not a solution either, as the high background respiration will interfere with the detection of the mostly very slow mineralization of the tested polymers.

In summary, new endpoints to follow degradation, but not only mineralization, as given, for example, by Pfohl et al. [96], should be considered in specific testing strategies for persistence assessment of polymers.

As a further point, the physical shape of polymers in standard tests has to be specified. Effects of particle sizes on biodegradation have been observed for (synthetic) polymers [3, 60, 79]. Garcia-Depraect et al. [97] show that regardless of the (synthetic) polymer the mineralization rate increases with decreasing particle size (higher specific surface area). This is an effect on the time of mineralization only but not on the absolute mineralization percentage at the plateau. This proves that particle size plays a major role in determining the degradation rate, i.e., the complete material cannot usually be attacked all at once if the particle is too large. This is for example important during surface erosion as a limiting sub-process. Consequently, for both natural and synthetic polymers, the surface area is an important factor for the biodegradation kinetic. Smaller particles or fragments

Table 2 Degradation Information for natural polymers and natural materials

Natural polymer	General aspects	Degradation result	Summary	References
Cellulose	Recommended reference substance for ISO tests (validity criterion > 60% in 6 month, results usually higher)	Data for different compartments (water, seawater, soil, activated sludge) available. Soil: Plateau at about 70% mineralization or higher	Relative fast degrading; (see general aspects)	Martin and Haider [58], Kögel-Knabner [25], Gómez and Michel [59], Chinaglia et al. [60], Pischedda et al. [61], Tosin et al. [62], Briassoulis et al. [63], Tyagi et al. [33]
Starch	Degradation rates may be dependent on concentration; decreasing up to 50% when the starch present is < 10% of the soil organic matter (SOM). Low starch concentrations, in combination with low activity of starch degrading organisms could lead to stabilisation of starch in the SOM fraction	Disappeared (only partly mineralized) within 35 days in soil after incubation. Other studies show high mineralization (>80%) in 12 weeks. Large fraction already degrades in soil within 3 days, but can take several weeks to year to be degraded entirely	Highly degradable. Biodegradation rate faster than for cellulose. Biodegradation asymptotic	Cheshire et al. [64], Martin and Haider [58], Kögel-Knabner [25], German et al. [65], Polman et al. [24], Tyagi et al. [33]
Hemicellulose	Easily hydrolysable polymers	Aqueous medium (ISO 14851): >80% in 10 days	Degradable	Dekker [66], Pérez et al. [67], Erdal and Hakkarainen [68]
Lignin	Lignin turnover in soils could be faster than that of the total SOM. Degradation is related to the nature of vegetation and land-use, but also to the climate and soil characteristics. Co-metabolism with easily degradable carbon sources (sufficient energy, nutrients, enzymes). Fungi such as basidiomycetes and white-rot fungi are the only organisms able to extensively biodegrade lignin	Laboratory: 19–60% degradation for 13 weeks to 2 years. Field studies; degradation up to 5 years. Other literature reported that lignin degradation takes years or decades	Slower degradation rates in comparison to cellulose or starch. Incorporation into SOM. Complex structure of lignin makes it recalcitrant to most degradation processes	Kögel-Knabner [25], Thevenot et al. [57], Datta et al. [32], Polman et al. [24], Tyagi et al. [33], Amelung et al. [48]
Cutin	Cutin is an extracellular polymer. Enzymatic hydrolysis (cutinase) as an important pathway	Many microorganisms can grow on cutin as their sole carbon source and produce extracellular cutin hydrolyzing enzymes. Fully hydrolyzed by soil microorganisms in a period of 3–8 months		Kolattukudy [69], Heredia-Guerrero et al. [70]
Natural rubber	Degradation of natural rubber is a slow process. Various bacteria are reported to be able to degrade natural rubber. Most likely microbial attack targets the double bond of the cis-1,4-polyisoprene chain (oxidation)	Degradation is proven in experiments with isolated bacterial cultures. However, no standard degradation tests are available in literature		Rose and Steinbüchel [36], Nguyen et al. [71], Joseph et al. [72], Berekaa et al. [73], Shah et al. [39], Borel et al. [74], Nanthini and Sudesh [75], Kasai et al. [76], Seidel et al. [77], Shah et al. [78]

have a larger surface area, and thus a higher probability to be attacked. For this reason, rate-determining is often, but not in all cases, the first step, i.e., fragmentation due to physical forces or due to enzymatic processes.

If hydrolysis and fragmentation into smaller particles is the slowest process before a polymer can be mineralized, this will determine the degradation kinetic in an ISO standard test system. Bioassimilation or assimilation into soil organic matter is a competing parallel process to mineralization but is currently not considered in standard testing. This is in contrast to chemical regulation in the EU, e.g., pesticide regulation, where bio assimilation or assimilation to the solid matrix is considered as "NER" (non-extractable residues). In current persistence assessment of non-polymeric substances, NER can be classified as degraded if assimilation in biota or solid matrix can be proven. Details on NER characterization has been communicated by ECHA [98] and corresponding procedures have now been published [99, 100]. Though these NER can only be determined using isotope labelled test substances (mostly ^{14}C-labelling) during laboratory testing, it could play a significant role for the fate of natural and synthetic polymers. The importance of soil organic matter is undisputed and one of the relevant, if not the most relevant, processes of humus formation is the assimilation of natural polymers.

In the environment, the absolute amount of natural polymers is a result of several influencing factors. Besides formation and biodegradation potential, environmental characteristics are also important. For natural materials such as wood, the degradation will be longer than for the polymer itself such as cellulose or lignin. The reason for this is the unfavourable surface to volume ratio and thus limited accessibility to be attacked by UV, water, temperature or microorganism. As soon as the natural materials are fragmented into small pieces (e.g., chipped wood, sawdust etc.) the degradation time will decrease.

However, wood and even leaves can exist in the forest under dry conditions for years after a tree has died and it is typically recycled by fungal degradation (Fig. 4). Certainly, even chipped wood will exceed REACh 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 has the function to protect woody cell walls against microbial attack [25]. Often slow degrading material contains some constituents which are hardly mineralized, and will be potentially incorporated into the biomass or humic substances. This must be considered for persistency assessment (see NER assessment above). As there is no doubt that humification is a process that generates new covalent bonds it could be considered, for example, like NER type II [98] in the current *P* assessment as "degraded".

Conclusion

The few results from available screening tests indicate that some natural polymers are readily biodegradable. However, other natural polymers are not biodegradable within a short time, which is a consequence of their intended function in nature. Even natural polymers, that degrade usually more rapidly, might be subject to stabilizing processes such as humification, where the polymer carbon is not mineralised but bound for hundreds and thousands of years. Those processes are of no environmental concern, and are the basis for soil genesis and crucial for life on earth.

Although data from simulation tests are missing, there is no doubt that many natural polymers must be considered as persistent, i.e., their degradation half-lives are above the persistence triggers given in Annex XIII of the REACh regulation [101]. Nevertheless, natural polymers are not considered an environmental concern, and this proves mineralization alone is not a resilient persistence endpoint, e.g., formation of stable (soil-) organic matter is an important result of the degradation of natural polymers as well.

Natural polymers are excluded from the ECHA restriction proposal for intentionally added microplastic by definition. This could lead to conflicts in testing where natural polymers are used as reference materials. Synthetic polymers that show similar or better degradability in those tests might have to be classified P while the slower degrading reference materials are considered "inherently" degradable.

As a result, it can be stated that new polymer specific parameters and endpoints are urgently needed to assess the persistence of synthetic polymers in the environment. The mineralization endpoint, which was introduced due to the lack of possibilities to analyze polymers in a complex environmental matrix, is alone not a reliable parameter to indicate the stability of polymers in the environment. In some cases, it even leads to contradictory results. Mineralization of any polymer—natural or synthetic—is a stepwise process. This should be considered in the evaluation and derivation of suitable persistence criteria, and in the weight of-evidence evaluation of the biodegradation potential of polymers.

For natural polymers, mineralization is recognized as not being a suitable endpoint and thus, it is overwritten by the "inherent" definition. This is not the best recommendation for a parameter to be used as the sole decision on the persistence of synthetic polymers, either. Depolymerization may be an alternative endpoint for primary degradation, whereas it to be discussed how

to consider the numerous numbers of transformation products. In addition, further parameters exist already in persistency assessment, e.g. NER assessment to consider assimilation of substances into SOM, and could serve as a blueprint for the development of polymer specific guidance.

Abbreviations

ASTM	American society for testing and materials
Da	Dalton
ECETOC	European centre for ecotoxicology and toxicology of chemicals
ECHA	European chemicals agency
EPA network	Network of the Heads of European Environmental Protection Agencies
EU	European Union
FTIR	Fourier-transform infrared spectroscopy
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
LMW	Low molecular weight
MP	Microplastic
NP	Nanoplastic
OECD	Organisation for economic co-operation and development
P	Persistent
PAM	Polyacrylamide copolymers
Pyr-GC/MS	Pyrolysis gas chromatography-mass spectrometry
REACh	Registration, evaluation, authorisation and restriction of chemicals
SOM	Soil organic matter
$ThCO_2$	Theoretical carbon dioxide evolution
ThOD	Theoretical oxygen demand
UBA	Umweltbundesamt
UVCB	Unknown or variable composition, complex reaction products or of biological materials
vP	Very persistent
WWTP	Wastewater treatment plant

Author contributions

Availability of data and materials
All data generated or analysed during this study are included in this published article. The authors declare that data supporting the findings of this study are available within the references given in the article. Further information is given in the reports from CEFIC LRI ECO 52 (https://cefic-lri.org/projects/eco52-bioavailability-complex-substances-and-overall-persistence-bcop-three-themes-to-deliver-a-step-change-in-persistence-assessments/).

Declarations

Ethics approval and consent to participate
Not applicable.

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Competing interests
The authors have no competing interests to declare that are relevant to the content of this article.

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