



A Review of Standards for Biodegradable Plastics

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Executive Summary

This review aims to provide information on the mechanisms of biodegradation, and why not all plastic is biodegradable. Additionally, it aims to illustrate why this is a complicated issue, and how suitable testing for biodegradability must be carried out carefully to avoid unintended consequences and encourage the development of high-quality biodegradable materials. Standards and legislation need to address risk but at the same time incentivise new product development.

A layman's glossary is included to assist the reader in understanding the technical terms often used when discussing the subject of bio-based plastics and biodegradability. The authors detail the differences between bio-based and oil-based plastics and the difference between biodegradable and non-biodegradable plastics.

When we ask "how biodegradable material is" we are really asking about the *rate* of its degradation in its environment – this depends upon both its chemical composition (what type of plastic) and where the material ends up at the end of its life:

- In controlled environments, such as anaerobic digesters, processes are managed and therefore standardisation of the timescales involved in biodegradation can be achieved and widely used⁴.
- Natural environments are much more complex. Many factors contribute to the environment in which materials may degrade, i.e. fresh water or salt water, landfill site and location within a landfill, deep soil or top soil.

Testing is carried out on virgin materials in controlled environments which rarely mimic the environment experienced by a material at its end of life.

Measurement techniques to assess biodegradability and the complex mechanisms by which plastics (bio)degrade in different environments are discussed in some detail.

If a product is to be classified as biodegradable, the testing thereof should be done on the product in its final form, not the raw polymeric starting material.

1: Glossary

This section is not intended to provide detailed formal, legal or scientific definitions of the terms but to allow the reader to understand some of the vocabulary used in the report, thereby increasing qualitative understanding. There is a common confusion between different definitions due to the similarity in terminology.

Bioaugmentation

The introduction of microorganisms to a polluted area, capable of degrading the pollutant (such as an oil-spillage, where oil may be degraded faster by addition of oil-degrading bacteria.)¹.

Biodegradable

A plastic (or a polymer) is considered biodegradable when it breaks down to basic elemental components (water, biomass and gas) with the aid of microorganisms.

Plastic may be degradable, but **not** biodegradable – for example, if it is degraded by light.

Biopolymers / Bio-based polymers

Polymers generated from natural monomers as formed by plants, microorganisms and animals. Can be either fully naturally derived or consist of a mixture of artificially synthesised and natural polymers.

They are often, but not always fully biodegradable depending on additives and composition².

Bioremediation

The purposeful use of microorganisms in optimised environmental conditions with additional microbial nutrients to breakdown pollutants (such as an industrial composting facility)¹.

Biostimulation

The modification of the environment, such as the addition of extra nutrients to a polluted area, to encourage microbial growth to aid in the breakdown of a pollutant¹.

Compostable

Requiring specific conditions for total degradation, either by control of the environment or removal of residual materials. Plastic may be biodegradable but not compostable. For example, if the plastic biodegrades but leaves behind toxic residues it would not be suitable for compost.

Degradation

A plastic (or a polymer) is considered degradable when it breaks down to smaller (monomeric) subunits and loses its original properties.

Microplastics

Very small (<5mm) **non-biodegradable** plastic particles formed through mechanical degradation of larger pieces of plastics. Biodegradable plastic should not yield microplastics as these will be assimilated by microorganisms.

Polymer

Made of many i.e. a material generated from multiple smaller building blocks (**monomers**). The final blend of polymers yields the material commonly referred to as **plastic**. The word “plastic” actually refers to the properties of the material rather than its composition.

2: Introduction

2.1: What are biodegradable plastics?

The same properties that make plastics an essential commodity in modern day life are also what cause an environmental problem. Since large scale plastic production was established, plastics have become ubiquitous with society becoming dependent on their use. Unfortunately, the ubiquity and durability of plastics have led to problems if waste plastic is inappropriately dealt with, invading natural habitats and causing harm to local ecosystems. Some areas have such high levels of plastic pollution that a new epoch has been coined relating to the levels of plastic in soil samples: the Anthropocene^{3,4}.

Recently, there has been a drastic change in public perception of plastic in the environment and there is a clear desire for improved management of plastics at the end of their useful life. One potential approach is to encourage the use of bio-based and biodegradable plastics. Historically there has been confusion around these terms – they are often incorrectly used interchangeably. While many bio-plastics are more amenable to biodegradation, it is important to realise that plastics such as bio-polyethylene are identical in chemical composition as polyethylene from petrochemical sources. The prefix “bio” relates only to the feedstock used to manufacture the material. As a result there is no difference in biodegradability between polyethylene and bio-polyethylene, however the latter is relatively carbon neutral, while the former is not (Table 1)⁵.

Table 1 – Classification of plastics. Adapted from reference ⁵. Note many plastics can be made from crude oils AND plant-based materials. Examples in this table are highlighted in **bold italics**. They are chemically identical so therefore have identical properties with respect to biodegradability.

	Bio-based plastics		Oil-based plastics	
	<i>Derived from plant-based materials</i>	<i>Example of use</i>	<i>Derived from crude oil</i>	<i>Example of use</i>
Biodegradable plastics	Poly(lactic acid) (PLA)	Medical	Poly(ε-caprolactone) (PCL)	PVC glue
	Polyhydroxyalkanoate (PHA)	Medical	Poly(butylene Succinate/adipate) (PBS/A)	Agriculture
	Polysaccharide derivatives	Food packaging	Poly(butylene adipate-co-terephthalate) (PBA/T)	Paper cups
	Poly(amino acid)	Medical		
Non-biodegradable plastics	<i>Polyethylene</i> (bio-PE)	Packaging	<i>Polyethylene</i> (PE)	Packaging
	Polyol–polyurethane	Tyres	Polypropylene (PP)	Packaging
	Polysaccharide derivatives	Food packaging	Polystyrene (PS)	Packaging
	<i>Poly(ethylene Terephthalate)</i> (bio-PET)	Water Bottles	<i>Poly(ethylene terephthalate)</i> (PET)	Water Bottles
			Polymethylmethacrylate (Perspex)	Optical materials and others

The vast majority of plastics are produced from non-renewable, petrochemical sources. Bio-plastics, as the name suggests, are derived from biological sources (they are often referred to as “plant-based” or “bio-based” plastics). For example, cellulose, the most abundant biomass material on earth, has been widely used as a bio-plastic. Cellulose can also be used in derivative forms, such as cellulose

acetate, to add other desirable characteristics like heat tolerance. However, these derivatives often remove the capacity for biodegradation in the environment^{5,6}.

Different plastics have different characteristics depending on their chemical composition. Plastics are made of many single building blocks, known as monomers. Monomers are linked to form long polymers which are the fundamental form of plastics. Differences in chemical structure, bonding and conformation within in these polymers are what give different plastics desirable characteristics².

2.2 The importance of definitions and understanding of complexity in biodegradation

Understanding the meaning of the term biodegradability is critical to understanding the issues involved:

- Biodegradability of plastics, as a starting point, can be described as the breakdown of plastic monomers or polymers due to biological processes.
- In the simplest terms, biodegradable materials can be converted to biomass, carbon dioxide (CO₂) and water. Methane may also be produced in anaerobic (low or zero oxygen) conditions (e.g. buried in landfill sites).

When we ask “how biodegradable material is” we are really asking about the *rate* of its degradation in its environment – this depends upon both its chemical composition (what type of plastic) and where the material ends up at the end of its life:

- In controlled environments, such as anaerobic digesters, processes are managed and therefore standardisation of the timescales involved in biodegradation can be achieved and widely used⁴.
- Natural environments are much more complex. Many factors contribute to the environment in which materials may degrade, i.e. fresh water or salt water, landfill site and location within a landfill, deep soil or top soil.

Testing the biodegradation properties of the material involves attempting to control these factors to better understand the materials, breakdown processes, timescales and products formed involved in its biodegradation.

A particularly influential parameter to biodegradability is the level of photodegradation which occurs before, during or even after biodegradation depending on the location. UV light breaks chemical bonds within the plastic polymer which can allow for faster biodegradation by increasing the surface area upon which enzymes can act. Plastics in deeper water or buried in soil are not exposed to UV light, and thus can require more time to biodegrade.

2.3: The physical and chemical properties of a plastic affect degradation

Plastics are typically designed for strength and resilience in direct conflict with their ability to (bio)degrade. The chemical structure of plastic materials means there are few mechanisms for biological catalysts (enzymes) to breakdown the polymer. Plastic degradation and biodegradation rely on several critical factors, summarised in Table 2 below⁷. These factors and more are covered in further detail in Section 4.1.

Table 2 – Chemical and structural factors affecting the degradation of plastics. Adapted from reference ⁷.

	Factor	Description
Surface conditions	Surface area	Area exposed to the environment for degradation reactions to occur
	Hydrophilic properties	Ability to mix with water
	Hydrophobic properties	Ability to repel water
First order structures	Chemical structure	Presence of specific chemical bonds or side groups
	Molecular weight	Mass of an individual polymer molecule
	Molecular weight distribution	Range of masses within a plastic material - plastics are not single, uniform molecules. They have a (controlled) range of molecular weights
High order structures	Glass transition temperature	The temperature at which a hard polymer transitions into a soft rubbery polymer.
	Melting temperature	The temperature at which a solid polymer becomes a liquid.
	Modulus of elasticity	Ability to resist permanent mechanical deformation.
	Crystallinity	Degree of structural order or disorder in a polymer.
	Crystal structure	Arrangement of individual molecules in a crystalline polymer.

2.4: Methodology for testing plastic biodegradability

Tables 3 and 4 detail some results from the literature on the rate of degradation of a range of plastics under various conditions.

The tables demonstrate the complexity of answering what appears to be a simple question: how long does plastic take to degrade? For example, pure PLA (polylactic acid) was measured to biodegrade completely (100%) in 28 days and also 13% in 60 days. The lack of standardisation of test methodology is at the heart of the (seeming) discrepancies. For example, note the range of temperatures used in the test results listed in tables 3 and 4.

Attempts to standardise conditions typically rely on carefully controlling temperature, humidity and other factors and thus control the rate of biodegradation. **A clear definition of biodegradability within managed (such as industrial composting facilities) or un-managed (open, natural eco-systems) is lacking.** The latter clearly has a much broader and complex range of factors affecting the degradation process⁴.

A recent publication from Harrison et al. (2018) is highly recommended for a thorough review of existing biodegradability standards in particular for plastic bags and films in aquatic environments⁴. One of the key conclusions was that while existing test procedures employ a reproducible method of determining biodegradation (i.e. by gas evolution as discussed in section 4.1), the data obtained can significantly underestimate the duration actually required within natural ecosystems. Partially this is because the test conditions themselves often mimic *synthetic* conditions rather than a dynamic open system. A key issue was identified in the lack of guidelines and methodological consistency for the analysis of different polymer types, composite materials and materials containing additives⁴.

The current testing methodologies have the potential to incentivise manufacturers to develop ‘biodegradable plastics’ which perform well in biodegradability tests, but then do not degrade appropriately when in the natural environment.

As will be clear after the following sections, the term biodegradation covers a complex process with several areas in need of increased clarity to provide appropriate standardisation.

3: Summary tables – examples of degradation rates and standards for biodegradation

Table 3 - Timescale for degradation of biodegradable plastics under various conditions [Adapted from reference 8]

Source of bioplastic	Name of bioplastic		Type of environment	Conditions	Biodegradability (%)	Length of time (days)	Reference
Biobased	PLA based	PLA	Compost	58 °C	13	60	9
		PLA	Compost	58 °C, pH8.5, 63% humidity	84	58	10
		PLA	Compost	70% moisture, 55 °C	~70	28	11
		PLA	Compost	Aerobic 58 °C, 60% humidity	60	30	12
		PLA	Synthetic material containing compost	Aerobic, 58 °C	63.6	90	13
		PLA	Synthetic material containing compost	58 °C	100	28	14
		PLA	Soil	30% moisture	10	98	15
		PLA	Inoculum from a municipal wastewater treatment plant	30 °C, aerobic	39	28	16
		PLA (powedered)	Soil	25 °C, 60% humidity	13.8	28	17
		PLA/PPP/starch (80/5/15%)	Compost	58 °C	53	60	9
		PLA/NPK (63.5/37.5%)	Soil	30 °C, 80% humidity	37.4	56	18
		PLA/NPK/EFB (25/37.5/37.5%)	Soil	30 °C, 80% humidity	43	56	18
		PLA/Soft wood (70/30%)	Compost	Aerobic, 58 °C, 60% humidity	40	30	12
		PLA/corn (90/10%)	Synthetic material containing compost	Aerobic 58 °C	79.7	90	13
		PLA/sisal fiber (SF) (60-40%)	Soil	30% moisture	>60	98	15
		PLA/PHB (75-25%)	Synthetic material containing compost	58 °C	100	35	14
	PHA-based	PHB	Soil	-	64.3	180	19
		PHB	Microbial culture from soil	-	~18	18	20
		PHB	Soil	Real conditions, temperature and humidity were measured regularly	98	300	21
		PHA	Soil	35 °C	35	60	22
		PHA	Soil/compost (90/10%)	25 °C, 65% humidity	40*50	15	23
		PHA	Soil	60% moisture, 20 °C	48.5	280	24
		PHB	Compost	58 °C	79.9	110	25
		PHB	Compost	70% moisture, 55 °C	~80	28	11
		PHB	Sea water	25 °C	80	14	26
		PHB	Sea water	Static incubation, 21 °C	99	49	27
		PHB	Sea water	Dynamic incubation 12-22 °C, pH 7.9-8.1	30	90	27
		PHBV	Sea water	Static incubation, 21 °C	99	49	27
		PHBV	Sea water	Dynamic incubation 12-22 °C, pH 7.9-8.1	30	90	27
		PHB	River water	Real conditions ~20 °C	43.5	42	28
		PHB	Brackish water sediment	32 °C, pH 7.06	100	56	29
		PHB	Marine water	28.75 °C (average temperature, pH 7-7.5)	58	160	30
		PHB/CAB (50/50%)	Soil	-	31.5	180	19
PHBV	Microbial culture from soil	-	~41	18	20		

	Starch-based	PHA/Rice husk (60/40%)	Soil	35 °C	>90	60	22
		Bioplastic (made from potato almidon)	Compost	Aerobic, 58 °C	~85	90	13
		Starch-based	Soil	60% moisture, 20 °C	14.2	110	24
		Mater-Bi bioplastic	Marine water with sediment	Room temperature	68.9	236	31
	Cellulose-based	Mater-bi bioplastic (60% starch 40% resin)	Compost	55% moisture, aerobic, 23 °C	26.9	72	32
		CA (from fiber flax)	Municipal solid waste mixture	-	44	14	33
		CA (from cotton linters)	Municipal solid waste mixture	-	35	14	33
	PA-based	Sponge cloth (cellulose-based)	Synthetic material containing compost	Aerobic, 58 °C	>80	154	34
		Nylon 4 (polyamides, bio-based)	Sea water	25 °C	80/30	25/21	26
	Petroleum based	PBS-based	Nylon 4 (polyamides, bio-based)	Composted soil	25 °C, 80% humidity, pH 7.5-7.6	100	120
PBS			Compost	Aerobic, pH 7-8, 58-65 °C, 50-55% moisture	90	160	36
PBS (films)			Soil	25 °C, 60% humidity	1	28	17
PBS (powdered)			Soil	25 °C, 60% humidity	16.8	28	17
PBS/soy meal (75/25%)			Compost	Aerobic, pH 7-8, 58-65 °C, 50-55% moisture	90	100	36
PBS/canola meal (75/25%)			Compost	Aerobic, pH 7-8, 58-65 °C, 50-55% moisture	90	100	36
PBS/corn gluten meal (75/25%)			Compost	Aerobic, pH 7-8, 58-65 °C, 50-55% moisture	90	100	36
PBS/switch grass (75/25%)			Compost	Aerobic, pH 7-8, 58-65 °C, 50-55% moisture	90	170	36
PCL-based		PBS/starch (films)	Soil	25 °C, 60% humidity	7	28	17
		PBS/starch (powdered)	Soil	25 °C, 60% humidity	24.4	28	17
	PCL-based	PCL	Inoculum from a municipal wastewater treatment plant	30 °C, aerobic	7.6	28	16
		Starch/PCL	Inoculum from a municipal wastewater treatment plant	30 °C aerobic	53	28	16
		PCL	Compost	55 °C	38	6	37

PLA = polylactic acid; PPP = poly(p-phenylene); NPK = fertiliser; PHA = polyhydroxyalkanoate; PHB = polyhydroxybutyrate; PHBV = poly(3-hydroxybutyrate-co-3-hydroxycalcerate); CAB = cellulose acetate butyrate; CA = cellulose acetate; PBS = polybutylene succinate; PCL = polycaprolactone.

Table 4 – Currently active biodegradability standards and test methods for all plastic materials in soil, marine and waste water environments [Adapted from ⁴].

Environment	Standard or test method	Inoculum	Medium	Temp (°C)	Measurement Type	Test Duration	Number of replicates	Validity criteria
Wastewater and sewage sludge	BS EN ISO 14851:2004	Sludge, compost and/or soil	Synthetic; aerobic	20-25 (±1)	BOD; static test conditions	Max. 6 months	Min. 2	Greater than 60% degradation of reference material; BOD of negative control must not exceed a specified upper limit.
	BS EN ISO 14852:2018	Sludge, compost and/or soil	Synthetic; aerobic	20-25 (±1)	CO ₂ evolution; static test conditions	Max. 6 months	Min. 2	Greater than 60% degradation of reference material; CARBON DIOXIDE evolved from negative control must not exceed a specified upper limit.
	BS ISO 13975:2012	Sludge, livestock faeces or other organic waste	Direct exposure to inoculum; anaerobic	35 ±3 or 55 ±5	CO ₂ and CH ₄ evolution, DIC; static test conditions	Max. 3 months	2	Greater than 70% degradation of reference material after 15 days; Extent of degradation (%) must differ by <20% between replicates.
	BS EN ISO 14853:2016	Sludge, livestock faeces or other organic waste	Synthetic; anaerobic	35 ±2	CO ₂ and CH ₄ evolution, DIC; static test conditions	Max. 3 months	Min. 3	Greater than 70% degradation of reference material; pH of the medium must remain between 6 and 8.
Marine	ISO 18830:2016	Sediment or sediment and seawater	Synthetic or natural seawater	15-28 (±2)	BOD; static test conditions	Max. 24 months	3	Greater than 60% degradation of reference material; BOD of negative control must not exceed a specified upper limit.
	ISO 19679:2016	Sediment or sediment and seawater	Synthetic or natural seawater	Synthetic or natural seawater	CO ₂ evolution; static test conditions	Max. 24 months	3	Greater than 60% degradation of reference material; CO ₂ evolved from negative control must not exceed a specified upper limit.
	ASTM D6691-09	Preselected strains or seawater	Synthetic; aerobic	30 (±1)	CO ₂ evolution; static test conditions	Max. 3 months	Not specified	≥70% degradation of reference material
	ASTM D7473-12	Seawater or combination of seawater and sediment	Direct exposure to inoculum; aerobic	Varies depending on <i>in situ</i> conditions	Visual evidence for degradation; loss of dry mass	Max. 6 months	3	Not specified
	ASTM D7991-15	Sediment and seawater	Direct exposure to inoculum; aerobic	15-28 (±2)	CO ₂ evolution; static test conditions	Max. 24 months	3	≥60% degradation of reference material
Soil*	ISO 17556:2012	Adapted or non-adapted soil	Natural Soil; aerobic	20-28 (±2)	BOD; CO ₂ evolution	Max. 6 months	Not specified	≥60% degradation of reference material. The measured CO ₂ or the BOD values from the blanks at the end of the test are within 20% of the mean.
	ASTM D5988-12	Adapted or non-adapted soil	Natural Soil; aerobic	20-28 (±2)	CO ₂ evolution	Max. 6 months	Not specified	≥70% degradation of reference material. The measured CO ₂ or the BOD values from the blanks at the end of the test are within 20% of the mean.
	NF U52-001	non-adapted soil	Natural Soil; aerobic	Not specified	Visual evidence for degradation	Max. 6 months	Not specified	≥70% degradation of reference material. Standard deviation of replicates <20%.

	UNI 11462:2012	non-adapted soil	Natural aerobic	Soil;	21-28	CO ₂ evolution	Max. 3 months	Not specified	≥60% degradation of reference material. Standard deviation of replicates <10%..
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BOD= Biological oxygen demand; DIC = Dissolved inorganic carbon; * = information derived from ³⁸.

4. Biodegradation of plastics

4.1 Basic chemistry of degradation

The same properties that make plastics an essential commodity in modern day life are also those that cause an environmental problem. Due to their inherent stability, some plastics can remain in the environment for hundreds of years and do not naturally degrade to a large degree^{4,39}. By designing the initial polymer more carefully however, the total lifetime (use time and in particular post-consumer use) of a material can be controlled and reduced. Some materials such as parts used in cars or planes, or in the building industry, need to be extremely stable over a long period and are designed to not degrade.

Other materials, however, such as single-use sachets and plastic bags, take-away boxes, plastic cups, bottles and cutlery can have their total lifetime divided into two: the usable lifetime and the degradation lifetime.

By designing the chemical composition and additives used in single use plastic products, both usable and degradation lifetimes can be controlled to enable rapid biodegradation at the end of the use.

At the molecular level plastics may be described as a backbone chain built from units (monomers) of mostly carbon.

The functional group (or side chain) of the individual monomer is the main contributor to the differences in the chemical and mechanical properties of plastic. These vary from simple carbon chains (e.g. polypropylene (PP)), to chlorine (e.g. polyvinyl chloride (PVC)) and complex sidechains (e.g. poly(methyl methacrylate) (PMMA)). In terms of biodegradation, the functional group is of critical importance, as some chemical groups and bonds are more easily degraded by biological agents.

The basic driving force of biodegradation is the use of the carbon (C) bound in the polymer as a feedstock for microorganisms to grow. Under aerobic conditions, this reaction can be simply summarised as:



Hence, the **biodegradation rate is usually determined by measuring the amount of CO₂** (carbon dioxide) evolved, **or the amount of C_{polymer} that has disappeared over time**. The theoretical total amount of CO₂ can be determined from the known input of C_{polymer}. Most legislation on biodegradability is based on a **percentage of the theoretical CO₂ produced over a given timeframe**. When oxygen is not available, methane gas (CH₄) is also produced which can also be measured.

This description, however, is a considerable simplification of a complex process, and this review aims to describe the complexity of biodegradation and address the challenges of developing an adequate laboratory-based test and subsequent guidance and legislation.

The timescale for biodegradation of plastic material is dependent on many factors, including the composition of the starting material (polymer chain length and strength of interactions, plastic

formulation and additives), the environment (soil, water, temperature, presence of microorganisms) and the shape of the material (surface area).

As described above, the chemical structure of the plastic influences stability. For example, in water at 25 °C, the half-life of the hydrolysable chemical bond within a polymer can vary from only 4 hours for used in drug delivery applications with which most of us are familiar e.g. common painkillers like paracetamol (poly(ortho ester) polymers) to common polyester bonds (such as used in PET-plastic drinks bottles) that can take 3.3 years. At the other extreme lie the resilient bonds present in various types of Nylon (polyamides) provide an estimated half-life at 83 000 years⁴⁰. Technically, these polymers can, in theory, still be classed as biodegradable as they will *eventually* degrade. The speed of these chemical reactions will vary with by environment and can be increased by the addition of catalysts.

4.2 Stages of degradation

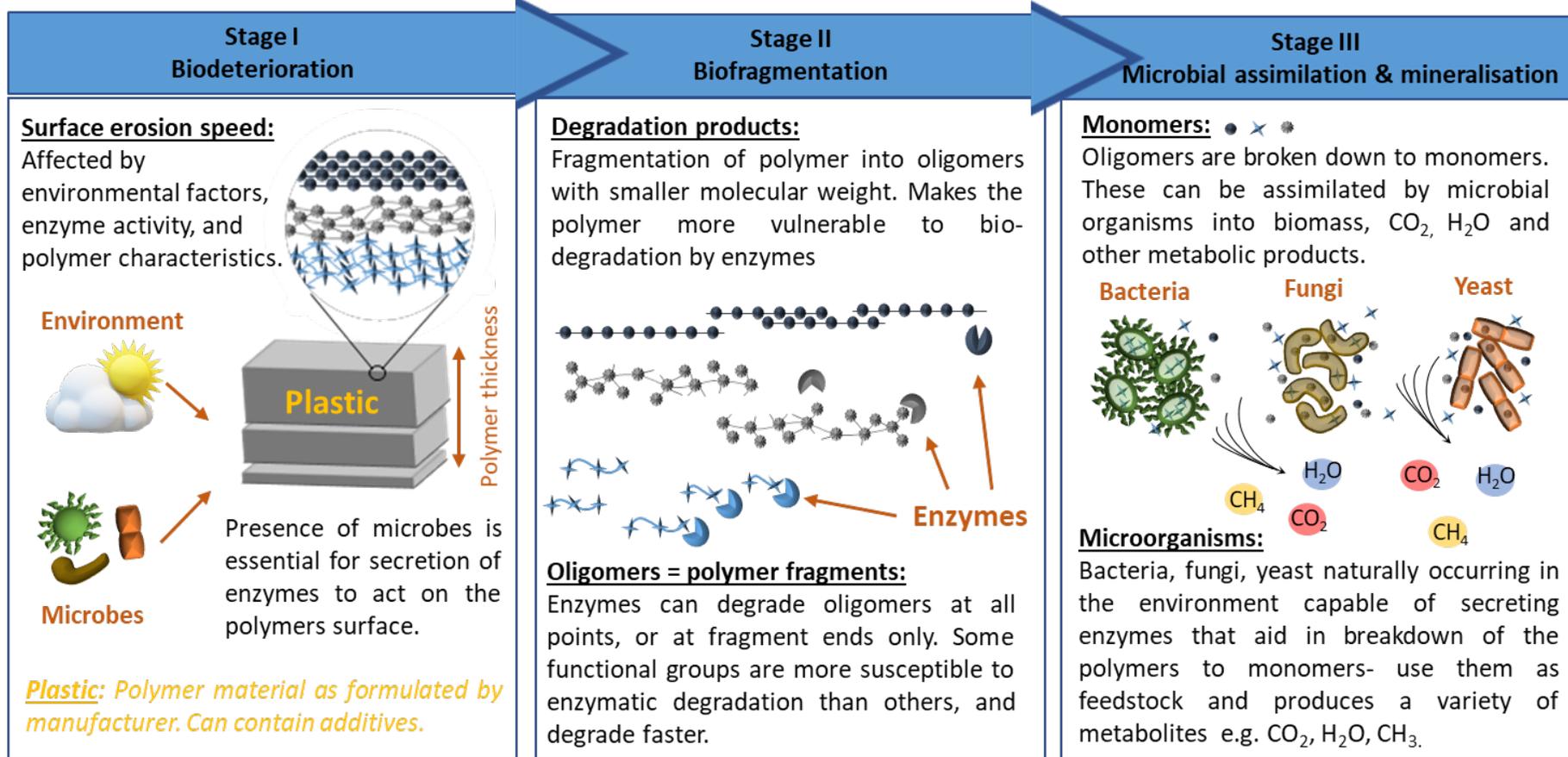
Generally, biodegradation occurs in three stages:

1. *Abiotic-deterioration and biotic-deterioration*
2. *Biofragmentation*
3. *Microbial assimilation and mineralisation*

Figure 1 summarises the processes occurring at **(a)** each of the three main stages of biodegradation. and **(b)** their corresponding gas development phases. Analysing gas development of CO₂ and CH₄ gives an indication of activity of the microorganisms. **(c)** Methods of testing the progress of biodegradation: loss of mechanical properties serves as a quantitative indicator of bio deterioration during early lag phase., visual inspection is used for qualitatively detecting changes in features and signs of disintegration (inspection under microscope can estimate microbial attachment) and mass loss is a quantitative approach that correlates with gas evolution- insensitive during early stages but can indicate bio assimilation at a later stage.

Figure 1 – Biodegradation summary

a



b

Lag phase

Biodegradation phase

Plateau phase

c

Loss of mechanical properties

Visual inspection and mass loss

Stage 1: Abiotic-deterioration and biotic-deterioration

This is the initial stage at the end of the plastics useable lifetime where the plastic begins to lose its physical and structural properties. It can be tested quantitatively by changes in the tensile and elastic strength and brittleness of the material.

Most initial degradation mechanisms can be considered *abiotic*, as they involve physical and chemical actions but not biological actions. They are a combination of several factors⁴¹:

- Mechanical degradation: Physical forces acting to damage plastic. Compression, tension and shear forces such as air and water turbulence, snow pressure, animal tearing etc.
- Light degradation (also referred to as photo-degradation): UV-radiation from the sun (or artificial light source) initiates chemical reactions to destabilise polymers.
- Thermal degradation (thermooxidative): Exposure to heat influences the organised framework of polymers.
- Chemical degradation: Exposure to chemicals such as atmospheric pollutants or agrochemicals can lead to a breakdown. Oxygen in the atmosphere is one of the most important factors to oxidative degradation of polymers, and dependent on the type of plastic, can disrupt several types of chemical bonds.

Biotic-degradation is defined as the breakdown of the polymer from the action of biological reagents i.e. enzymes from microorganisms.

Often, both the abiotic and biotic mechanisms act synergistically to break down a polymer, but many plastics are inherently *biologically un-reactive*. These rely on the initial abiotic (mechanical) degradation to facilitate the next stage of biodegradation and may require other reagents (see below in section 5 for further discussion regarding additives) to speed up chain reactions of fragmentation⁴². Once a polymer is broken into smaller fragments (oligomers) it is often more vulnerable to biotic degradation as described in Figure 1.

In plastic degradation studies, heat exposure and UV-light is frequently used at exaggeratedly high levels to speed up the mechanical abiotic degradation before testing the biodegradation time scale. This artificial pre-treatment can vary between studies and affects the final results. Unfortunately, Exposure to conditions found in nature means a study would take years to complete.

In order to keep testing cost-efficient and not be a hindrance for the development of new products, pre-treatment - the exposure to artificially high mechanical degradation - is necessary, but is lacking standardisation.

The rate of the initial breakdown also depends on many other factors including (but not limited to) the polymer chain length, crystallinity, molecular weight distribution, the size, shape and geometry of particle, the surface porosity, pore size and distribution, pore geometry and water diffusivity in the polymer matrix – all of which are function of the polymer's manufacturing process. These factors will not be discussed here, but are covered in great detail by Colwell *et al.* (2017), where mathematical models for degradation calculations are also reviewed⁴⁰.

Stage 2: Biofragmentation

As mentioned, once a plastic polymer fragments into shorter chains (oligomers), it becomes more vulnerable for enzymatic (ie bio) 'attack'. The bioavailability of the material increases as it is both physically and chemically more accessible to the action of microorganisms and the enzymes secreted by them⁴⁰.

The enzymes can be released to their surrounding environments by microorganisms to work directly on the polymers, or the microorganisms may rely on abiotic factors to break the polymer into sufficiently small pieces to allow them to enter the cell to be hydrolysed by internal enzymes^{42,43}. The rate of breakdown depends on the nature of the polymers. Linear non-reactive fragments will be harder for the enzymes to access and disrupt, compared to polymers with several functional groups that present a handle for the enzymes to act on.

Another rate-determining factor is the quantity of enzyme available, which in turn depends on the microorganisms present. This is further discussed below, but put simply, the more microorganisms that can degrade the plastic, the faster it will degrade. Several studies suggest that bioaugmentation (addition of more microorganisms) targeted to enhance the rate of biodegradation and a range of microbial hosts have been identified as degrading plastics such as PLA, LDPE, PET, and several other polyesters⁴⁴⁻⁴⁸.

The fragmentation stage can be difficult to assess in a quantifiable manner and is mainly tested for by **visual inspection** such as microbial attachment to plastic fragments, or by mass loss. The visual inspection typically requires a microscope and computational analysis to avoid bias.

As more polymers are hydrolysed, gases begin to develop and can be detected and quantified to indicate the final stage of degradation.

One major problem is that the mechanical breakdown of plastic while leaving the polymer more vulnerable to microbial degradation, can also result in the formation of potentially non-degradable micro-fragments known as micro plastics¹². Problems associated with microplastics are further discussed in Section 6.

It is important that the degradation process does not stop at fragmentation as this results in accumulation of microplastics.

Stage 3: Microbial assimilation and mineralisation

This stage can be viewed as the microorganism "eating" and "digesting" the polymers for their own growth and energy needs.

The final stage of biodegradation is the assimilation of the monomers into a microorganism to generate cellular biomass and carbon dioxide or methane depending on availability of oxygen (effectively air). Conditions with plenty of oxygen are described as aerobic, limited oxygen as anoxic and no oxygen as anaerobic). The rate of this stage can mostly be quantified by measuring gas evolution, or if a reaction is performed in a bioreactor, by increases in biomass of the chosen microorganism⁴.

Some microorganisms (e.g. fungi) cannot metabolise plastics under anaerobic conditions, while other microorganisms *require* anaerobic conditions⁴⁹. Aside from oxygen, other environmental factors will

affect both fragmentation and microbial degradation rate, such as pH, temperature, moisture content etc.

The microorganism and environmental conditions at the final degradation site can vary greatly and influence the rate of biofragmentation of a plastic.

Table 5 summarises some of these factors and their challenges in different environments.

Table 5 – Summary of environmental factors affecting the rate of microbial assimilation of plastics.

Environment	Degradation
Fresh water or salt water	Plastic floating on the surface is exposed to moderate temperatures, UV light and oxygen from the air ⁵⁰ . This may speed their abiotic degradation. In deep waters photodegradation and thermooxidative degradation are reduced due to UV availability and oxygen supply limitations and relatively low temperatures ⁵¹ . The hydrolysis rate of polymers in saltwater is affected by lower microorganisms concentrations ⁵² , and dependent on the ability of the organisms to stick to the polymer surface.
Soil	Plastic buried in the soil is not exposed to UV rays from the sun necessary to photodegradation initiating further degradation ⁵³ . Some studies suggest that the photodegradation is a chain reaction and the degradation can continue in polymers in the ground after exposure to UV-light ⁵⁴ . Degradation results from the action of naturally occurring microorganism, which can vary for different soil types ⁸ . In deeper parts of soil anaerobic conditions limit thermooxidative degradation ⁷ .
Landfill	Limited availability of UV light and oxygen. Dark and anaerobic environment decreases the photodegradation and thermooxidation rate ⁵⁵ . Anaerobic conditions will favour the production of methane along with carbon dioxide. As a greenhouse gas methane traps 28-fold more heat per unit mass than carbon dioxide.
Composting facilities	Plastic is degraded by customised cocktails of microorganisms under optimised conditions ⁵⁷ . Bacteria preferably digest soluble nutrients, and most plastics are non-liquid ⁵⁸ . Plastics are deficient in essential elements (e.g. nitrogen, potassium, phosphorous) which are necessary for bacterial metabolism. This creates a need to add fertilisers in order to facilitate the degradation process ⁴³ .

The rate of degradation is dependent on the number of cells available to degrade the material⁵⁹. This, in turn, depends on the environment where the plastic ends up after its usable lifetime, i.e. the final degradation site of the material. This can vary from a landfill site or a waste-treatment plant to the natural environment such as waterways (both freshwater and saltwater) or hedgerows.

A varied blend of active microorganisms is more likely to facilitate rapid biodegradation of environmental plastics compared a single type of microorganism.

In an external, uncontrolled environment, whether “natural” or “man-made”, a mixture of different species of bacteria, yeast or fungal organisms are present and may work synergistically to speed up degradation processes. However, in a laboratory setting, the organism cultivated in a bioreactor to breakdown plastics can vary from a single type of microorganism to an inoculum from wastewater sludge or compost soil.

A study aiming to identify PLA degrading bacteria from manure compost succeeded in isolating four different strains capable of using PLA as a single carbon source⁴⁵. While this indicates that plastic degrading bacteria may be present in many environments, it also required several rounds of selection to isolate them from a nutrient-rich manure source. This highlights that most naturally occurring organisms will have a preference for more easily degradable carbon sources present in the soil before the breakdown of plastic becomes a necessity for bacterial survival. It also cannot be expected that a microorganism used in a biodegradation study will be prolific at the final degradation site for the plastic material.

For plastic ending in open uncontrolled ecosystems, degradation depends on the type and concentration of microorganisms present. Standardisation of the types of organisms (single and mixed) is lacking.

If the plastic is the only carbon source available for microorganism growth a lab test may show a higher rate of degradation compared to an unmanaged open environment where several other carbon sources may be available, and preferential, for the microorganisms.

4.3 Comments on the complexity of biodegradation

Biodegradation vs mechanical, abiotic degradation

Not all plastics degraded in the environment are biodegradable. In many cases, biodegradable plastics are confused with polymers being degraded in the environment under different physical conditions. Both cases are classified under the broader category of environmentally degradable polymers⁶⁰. According to ASTM and ISO, there are three main classes of environmentally degradable plastics:

- *Degradable plastic.*
 - Significant changes in the polymers chemical structure leading to a loss of some of its properties. The decomposition is triggered by specific environmental conditions, excluding the naturally occurring microorganisms. The end product is very small

fragments of plastic (microplastic). The effect of the accumulation of microplastic in nature and the risk of it entering the food chain is discussed in Section 6.

- *Compostable plastics*
 - Decomposition results from biological processes, involving customised mixtures of microorganisms. Compostable plastics degrade to carbon dioxide (CO₂), water and inorganic compounds without leaving traces of visually distinguishable or toxic residues, but require controlled conditions.
- *Biodegradable plastic.*
 - The decomposition process is carried out by naturally occurring microorganisms such as bacteria, fungi, and algae. The material should be fully assimilated, leaving no residues in the natural environment.

It is necessary to clearly distinguish between the different degradation pathways and so make the appropriate waste route obvious to the consumer/final user.

It is obvious that plastic that degrades into microplastics should be prevented from entering landfills or waterways, as the incomplete degradation process leads to accumulation of highly mobile microplastics in the environment⁶¹.

The rate of deterioration (stages 1 and 2) will differ from the rate of assimilation (stage 3)

The focus of current standards framework focuses on the rate at which a polymer becomes assimilated (stage 3) rather than the rate at which the polymer loses its mechanical properties (stages 1 and 2), see for example ISO14855.1:2012. *Determination of the ultimate aerobic biodegradability of plastic material under controlled composting conditions – Method by analysis of evolved carbon dioxide*. This poses some problems for oxo-biodegradable plastics. The later stages of biodegradation for even highly oxidised polyolefins occur at a much slower rate than for the benchmark of cellulose which is more rapidly assimilated by microorganisms. Alternative legislation circumventing this can be found in the French Standard: AFNOR-AC T51-1808. *Assessment of oxo-biodegradability of polyolefinic materials in the form of films*⁶².

Standards relating to defining how rapid a material biodegrades should take into account both the rate of initial degradation and fragmentation, as well as the final bio-assimilation.

For some applications, such as crop propagation films in agriculture, the deterioration rate can be of greater importance than the rate at which a material is fully assimilated⁶². This will be especially important depending on the application of the material, and the most likely final degradation site⁶³.

A variety of standards is required dependent on the timescale of degradation. For instance, single-use materials such as perishable food packaging should not need a lifetime much longer than that of the food it contains (for example ten-fold longer). Other materials such as carrier bags or plastic cups would need a slightly longer lifetime as to not start degrading while being held in storage but still degrade rapidly and fully after release into the environment.

Different levels of biodegradation rate and standards should be implemented depending on the expected lifetime of a product.

Physical form affects biodegradation

As biodegradation reactions mainly occur on the surface of a plastic, the ratio of the surface area to total volume is one of the most significant factors determining the rate of biodegradation.

The rate of degradation increases with the available surface of polymer⁵⁹. For example, in one study the maximum rate of fo degradation was measured to be 97 mg C_{polymer} per day. However, the study was carried out using finely milled, pure, virgin polybutylene sebacate. The authors recognised the limitations of applicability of their data for plastics not in nano-particulate form. The rate of degradation of real plastics in real environments is likely to be considerably lower.

Testing recycled plastics

If a product is to be classified as biodegradable, the testing thereof should be done on the product in its final form, not the raw polymeric starting material.

Plastic recovery and recycling should be part of any plan to tackle plastic waste. Recycled plastic is typically lower quality plastic consisting of dozens of types of different polymers with multiple contaminants due to the practical and economic restraints of sorting waste.

The biodegradability of material generated from recycled plastics, and not just virgin plastics, could be further characterised and investigated, as currently, very little information is available on the degradation of recycled plastics⁶⁴. As these plastics often consist of a blend of polymers and may have had stabilisers and other reagents added during the recycling process, the variety of interactions within the components of recycled plastic is considerably more complex than that of plastics generated from virgin material⁴⁰. Some information is available on the abiotic degradation of some of these mixed blend materials, suggesting that they are more stable against photo- and mechanical degradation than virgin plastic. This will slow down the rate of biodegradation. Likely the slower initial stage is due to the presence of anti-ageing additives and stabilising reagents making different types of polymers compatible^{62,65}.

Environmental pollution of plastics is not likely to consist of one type of polymer. Testing of biodegradability of mixed plastic waste within mixed populations of microorganisms is more likely to mimic a real-life-scenario than testing at the discrete levels.

Metrology for (bio)degradation

Methods for quantifying the degradation of plastic materials can vary between studies and can make the comparison of results problematic. Additionally, some of the testing methods require a stricter laboratory set-up, challenging the mimicking of a natural environment. Table 6 below summarises the different methods of measuring biodegradation and comments on the issues for each.

Table 6 – Summary of metrology methods for degradation of plastics.

Method	Comments
Visual inspection	Highly subjective, and should be performed using automation and validated software.
Mass loss	The simplest method to determine loss of material. Only possible with larger pieces of plastics at the earlier stages of degradation and does not account for the fate of the lost material (eg assimilated by microorganisms or abiotically degraded to microplastic)
Gas formation (carbon dioxide and/or methane)	Aerobic conditions should allow complete conversion to CO ₂ . Fully anaerobic conditions will result in the formation of a CH ₄ / CO ₂ mixture. Environmental conditions are likely to be neither fully aerobic or anaerobic. This method also does not account for the final fate of any additional components of the material such as additives which are not converted to carbon dioxide or methane
Biomass growth	Only useful when the plastic is the only carbon source in highly controlled environments.
Soil analysis	A more expensive and time-consuming analytical method to account for the fate of any additives or microplastic generation that may also be generated.

The theoretical yield of carbon dioxide can be calculated based on the known amount of plastic (and therefore carbon) used in a study. However, this does not necessarily take into account changes in enzymatic activity. Some enzymes are more likely to breakdown polymers towards biomass accumulation rather than carbon dioxide development, especially under varied oxygen availability. One study found it was possible to generate LDPE-based material that almost completely biodegraded in soil within two years with a very low risk of plastic fragments remaining in soil indefinitely⁶⁶. After two years of biodegradation experiments, the carbon was overwhelmingly converted to carbon dioxide and only a small amount converted to new biomass⁶⁶.

While the majority of a material may be found to degrade and be converted to carbon dioxide or methane within a reasonable timeframe, thereby passing the requirement for biodegradability, the remaining material may persist in the environment as plastic or microplastic and be unaccounted for.

Ideally, though not always practically possible, the fate of all of the plastic material should be accounted for in a biodegradation study (including additives).

Variation in testing

Current testing methods for biodegradability, outlined for marine and wastewater environments as outlined in Table 4, are insufficient as they lack standardisation. This leads to difficulties in comparing research results for plastic biodegradability by different investigators, thus making the consensus for biodegradability time scales hard to identify. Some of the issues between testing methodologies are identified below:

General conditions

- Temperature ranges (15-55 °C).
- Incubation times (3-24 months).
- Sources of microorganism inoculum.
- Oxygen conditions.

Plastic form

- Particle sizes and sources

- Origin of plastic i.e. newly produced material, used as appropriate (end of a lifetime) or removed from the environment (e.g. recovered from the sea).
- Pre-treated (e.g. with heat or light).

Validity criteria

- Percentage degradation (can vary from 60 – 90 % degradation).
- CO₂ production limits.
- pH stability.

Measurement type (also further discussed below)

- Visual (open to interpretation or requiring microscope and standardised analytical software).
- Gas production (requiring appropriately validated equipment).
- Monitoring of biomass if the plastic is the only carbon source.

Methods for testing biodegradability should (as far as practically possible) be standardised and validated to allow for comparison between different types of plastics degradability as investigated by different laboratories.

Laboratory conditions compared to unmanaged ecosystems

A laboratory-based test is far more controlled than real-world scenarios. Plastic may show good degradation qualities within the laboratory setting, but fail to degrade appropriately in a natural environment due to lack of an appropriate microorganism, or changing conditions at the final degradation site. Conversely, plastics having their biodegradability assessed outside the laboratory cannot be as carefully measured and may, therefore, fail criteria for biodegradability.

Harrison et al. (2018) discuss this issue, stating that even when biodegradation within a given environment has been partially demonstrated, many investigators still regard long-term (complete) biodegradation as an unresolved issue⁴. They mention that standards and specification often include a warning on the need for additional corroborative studies to demonstrate an acceptable degree of biodegradability in the open environment. However, no standards appear to give any guidance on how that corroborative work should be completed.

It is vitally important that standards based on laboratory conditions do not incentivise the development of plastics which perform well in tests but do not degrade appropriately in the environment.

Laboratory conditions cannot mimic a natural, unknown environment and as far as practically possible, a materials biodegradability should be tested both under more controlled, measurable conditions as well as in an unmanaged eco-system.

5. Effect of additives and implications in the environment

In order to enhance their macroscopic properties (e.g. stability, colour, texture), plastic polymers are rarely used in pure form in a product. Additives are incorporated into the product and therefore also released in the environment during degradation⁸. While increasing susceptibility to photodegradation and thermo-oxidation can help stimulate biodegradation of the material, the impact of a product's additive composition⁵⁰ on degradation and the final fate of the additives should be considered when conducting research into plastic degradation⁶⁷.

The lifetime of plastic material can be somewhat controlled by additives like pro-oxidants. Usually, these types of oxo-biodegradable materials have a proprietary formulation and additives consisting of metals salts. These are activated by light (photo-sensitive) or heat (thermal activation) to catalyse abiotic polymer bond degradation. Depending on the composition and concentration of the additives, the timing of activation can be controlled to an extent. The chemical changes in the polymeric structure make the material available for environmental microbes to begin biodegradation, speeding up the breakdown of the material⁶⁸.

Various research has investigated the nature and speed of degradation caused by the abiotic pre-treatment of the oxo-biodegradable materials. The majority of these studies are performed under accelerated conditions, mimicking sunlight using UV-lighting and incubation at increased temperatures to initiate mechanical breakdown^{54,66,69–73}. These have raised a number of key findings: one finding suggested that one of the main factors controlling the degradation is the type of pro-oxidant, rather than the actual type of polymer⁶⁸; whilst others have indicated that the length of time the plastics were exposed to radiation had a more significant effect than the intensity of the radiation and that increasing temperature increases the deterioration rate^{72,73}. More practical findings suggest that once activated, chemical breakdown by the oxidants will continue even in the dark⁵⁴. This is a crucial property, as disposed material may well end up buried.

Additives are usually a mixture of metal salts. One study testing thermo- and photo-degradation of LLDPE with the additives cobalt stearate, manganese stearate, or iron stearate found the latter to have the most desirable properties⁷⁴. While most of the metals used in the additives are naturally occurring in small amounts, an accumulation and increase in the concentration of certain additives can potentially become toxic. For example, the above study also found that a high concentration of cobalt slowed down the rate of subsequent bacterial degradation as the cobalt had a toxic effect on the microorganisms⁶⁸. The environmental impact of polymer residues and the risk of the potential accumulation of toxins should be fully investigated and clarified in standards to ensure that product degradation does not lead to negative environmental impacts⁷².

Additives can have a positive effect and increase the speed of biodegradation, but the fate of the additives should be clarified. Accumulation of additives may be harmful.

Essentially, additives allow for an accelerated mechanical (abiotic) breakdown of plastic. As discussed, this leaves the polymer vulnerable to microbial degradation and is a desirable property for most biodegradable plastic. However, it can be problematic when it also results in the formation of micro-fragments (microplastics), especially if these fragments are not ultimately biodegradable⁶⁸. Microplastics have begun to accumulate in the environment, and the consequences of this are not fully yet understood. This is further discussed in section 6.

Accelerated abiotic degradation should only be done for plastics that can also be fully assimilated by microorganisms to avoid accumulation of non-degradable microplastics.

6. Microplastics

Although the above review is mainly focused on the issues related to biodegradation of plastic, the growing concerns around microplastic accumulation merit a brief discussion here to put the issue and terminology into context with biodegradability. The key point is that while non-biodegradable plastics in the macroscopic form are an obvious environmental issue – and one that we can clearly see with our own eyes – microplastics derived from non-biodegradable polymers may be creating future health and environmental hazard which has yet to unfold.

Microplastic can be introduced into the environment directly from, for example, cosmetic beads and clothes fibres from laundering, or indirectly via breakdown of larger plastic pieces (mechanical degradation). If derived from non-biodegradable plastics these microplastics cannot be assimilated by microorganisms or digested by larger organisms. Due to their small size, they are easily consumed by a range of organisms at almost all food chain levels particularly in the marine environments e.g. zooplankton, coral, fish, birds and marine mammals⁷⁵. The plastic accumulates in their bodies, triggering physical effects such as satiation, which limits further nutrition, leading to starvation and death.

Additionally, microplastic tend to act as carriers for hydrophobic organic compounds (e.g. polychlorinated biphenyls (PCBs), pesticides and fertilizers) which accumulate within their porous structure⁷⁶. Consequently, it is not only the microplastic that enters the food chain but also the toxic chemicals which can be desorbed in the anaerobic environment of the gut and absorbed by animal tissues⁷⁷. Contaminants such as these can potentially alter physiology and behaviour. The current state of knowledge does not provide a definitive explanation of how they interact chemically and physiologically with various organisms (including humans)⁷⁸.

Importantly the ingestion of microplastics, whether carrying these concentrated toxins or not, means the plastic will eventually bioaccumulate up the food chain and enter the human diet. Recent results examining human stool have indeed found all test subjects to have ingested microplastic⁷⁹. As some of these fragments are small enough to enter the bloodstream, the health implications of accumulation of microplastic are potentially serious, but not fully understood or studied.

7. Conclusion

There is currently unprecedented public focus on the problems with plastics and the environmental impact of the accumulation of plastic. Little comment is made on the value of plastic to our lives and economy – for example, food packaging is viewed as almost universally bad with little consideration of the benefits of preventing food waste and thus reducing carbon emissions. Several major news outlets have whole sections devoted to news in plastic, and debates on how to reduce consumption can be found in all public forums. Documentaries such as Blue Planet (BBC) have encouraged the public to demand action. The UN^{80,81}, EU⁸² and the UK government⁸³ along with most other countries are looking towards environmentally suitable alternatives to conventional plastics.

Hence, there is a need for further clarification as to what plastics are truly biodegradable, under what conditions.

This review aims to inform on the mechanisms of biodegradation, and why not all plastic is biodegradable. Additionally, it aims to illustrate why this is a complicated issue, and how suitable testing for biodegradability must be carried out carefully to avoid unintended consequences and encourage the development of high-quality biodegradable materials. Standards and legislation need to address risk but at the same time incentivise new product development.

Summary boxes throughout the document highlight the most critical issues which are summarised below:

- Laboratory testing cannot recreate the natural environment. Several factors influence the rate of biodegradability and will generally be artificially imitated in a laboratory testing scenario.
- Some factors such as mechanical deterioration and temperature can be mimicked to a high degree of similarity with the natural environment. However, the types and concentrations of microorganism are much more complicated.
- Variation in rates of deterioration and assimilation stages of biodegradation can make it difficult for some plastics to obtain biodegradable status. It may be worth considering allowing a different category for slower, but still fully biodegradable plastics.
- The method of determining biodegradability is largely reliant of the development of gas from the material over time. This method may not take into account the environmental fate of any other components of the plastic, such as additives, or final polymeric components that cannot be further biodegraded.
- While simply exposing plastic to the environment may be the best method for demonstrating true biodegradability, this also greatly complicates the methods for clearly determining the rates and the full assimilation of all material.

- The public need to understand that biodegradable and compostable are related but different, especially for consumers to be aware of the best method of disposal as industrial composting facilities are not the same as natural degradation.
- Testing of material needs to be done on the product in its final form including additives.

In addition to the information obtained from literature, recent discussions between industry and academic groups as facilitated by IBioIC and ScotCHEM (held in Glasgow on 12-12-18) identified issues that could be resolved. Aside from a general lack of clarifications and definitions on biodegradability, the following issues were identified.

- There are currently no appropriate testing facilities available within the UK. Industry partners have to outsource testing to companies abroad in order to get appropriate data on the biodegradability of newly developed materials.
- The cost of testing facilities often is a disincentivising factor for the development of new materials. The lack of availability of anaerobic equipment was highlighted as a particular concern.
- A shared understanding of definitions within the subject was lacking, which would be helped by appropriate clarifications and standardisation.

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