

**BIODEGRADATION AND ENVIRONMENTAL IMPACT OF OXO-DEGRADABLE AND
POLYHYDROXYALKANOATE AND POLYLACTIC ACID BIODEGRADABLE PLASTICS**

Prepared for: the Parliamentary Commissioner for the Environment

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GLOSSARY

Abiotic	A chemical or physical process occurring in the absence of life or biological activity
Aerobic	A process occurring in the presence of oxygen
Additives	Chemical substances added to plastic polymers to provide them or enhance specific properties during their manufacture or use
Anaerobic	A process occurring in the absence of oxygen
Antioxidant	A substance that inhibits oxidative degradation
ASTM	American Society for Testing and Materials
Bio-based	A material or product partly derived from biomass or plant-based material
Biodegradability	The breakdown of organic compounds by microorganisms in the presence of air to produce carbon dioxide, water, mineral salts and biomass, or in the absence of oxygen to produce carbon dioxide, methane, mineral salts and biomass
Biodegradation	degradation resulting from the action of naturally occurring microorganisms
Bioerodible	a plastic material that is insoluble in water but can be converted into one that is water-soluble
CEN/EN	European Committee for Standardisation
Composting	A managed process involving biological decomposition and transformation of biodegradable material to produce carbon dioxide, water, minerals, biomass, and organic matter (compost or humus)
Degradation	A chemical change to the structure of polymers that produces a change in its chemical and/or physical properties
Ecotoxicity	The study of the field of ecotoxicology (a hybrid of ecology and toxicology), refers to the potential for biological, chemical or physical stressors to affect ecosystems
Ester	a chemical compound derived from an acid (organic or inorganic) in which at least one –OH (hydroxyl) group is replaced by an –O–alkyl (alkoxy) group
Disintegration/ Fragmentation	The physical breakdown of a material into very small fragments
Hydro biodegradable	a degradable plastic in which the degradation results from hydrolysis

Hydrolysis	chemical decomposition by which plastic polymers are split into smaller molecules by reacting with water
ISO	International Organisation for Standardisation
Mineralisation	the biological process whereby organic compounds are chemically converted by microorganisms to simple organic compounds or inorganic nutrients (methane, carbon dioxide, water, etc.)
MP	Microplastic, small pieces of plastic residue less than 5mm and larger than 0.3mm length in any dimension
Oxo-additives	see prodegradants
Oxo-degradation	A series of chemical reactions in which long polymeric chains are cleaved and broken into shorter lengths by the action of oxygen, UV light and/or heat
PE	Polyethylene, fossil fuel derived polyolefin plastic
PHA	polyhydroxyalkanoate plastic, bio-based and biodegradable
PHB	Polyhydroxybutyrate plastic, a type of PHA plastic
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), a type of PHA plastic
Photo-degradable	A plastic capable of being decomposed by the action of light, especially sunlight
Photolysis	A chemical reaction produced by exposure to light or ultraviolet radiation
PLA	Polylactic acid plastic, bio-based and biodegradable
Plastic	A material that contains as an essential ingredient one of more organic polymer substances of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or processing into finished articles, can be shaped by flow.
Polymer	Synthetic or natural large molecules, or macromolecules, composed of many repeated subunits
PP	Polypropylene, fossil fuel derived polyolefin plastic
Prodegradant	a chemical substance that catalyses the degradation of plastic

EXECUTIVE SUMMARY

This report reviews the scientific literature related to the biodegradability of oxo-degradable and biodegradable bio-based plastics and their potential impact in the environment. Due to their predominant use in high-volume single-use consumer products such as plastic bags and packaging materials, this review specifically discusses oxo-degradable polyethylene (PE) and polyhydroxyalkanoate (PHA) and polylactic acid (PLA) based biodegradable plastics.

Aims and methodology

The aims of this review are to:

- define the major classes of biodegradable plastics and discuss the chemical composition of the three predominant kinds, biodegradable PHA and PLA based plastics, and oxo-degradable PE plastics.
- outline the descriptions and definitions commonly used to describe oxo-degradable and biodegradable plastics, and the processes by which they can degrade and biodegrade
- summarise standard methods typically employed to assess the biodegradation of plastics
- describe the processes by which biodegradable and oxo-degradable PE plastics degrade, the chemicals they are transformed into, and chemical additives they may subsequently release
- describes standard methods used to assess the toxicity of residual materials produced by the biodegradation of biodegradable and oxo-degradable plastics, their limitations, and alternative new ecotoxicity approaches for assessing a wider range of potential impacts

This review summarises information obtained from a comprehensive review of peer-reviewed scientific papers and reports published by reputable organisations on the degradation and biodegradation of plastics.

Key issues

The most pressing issues about biodegradable and oxo-degradable plastics are the extent to which they degrade and biodegrade in the environment, and the timeframe in which this occurs. These issues are critical to determining if biodegradable and oxo-degradable plastics, and the substances they produce, are likely to accumulate and exert an impact in the environment.

The numerous scientific papers and reports summarised in this review clearly demonstrate biodegradable plastics composed of bio-based PHA and PLA polymers are readily degraded and biodegrade to benign chemicals during industrial composting. Biodegradable plastics produced from PHA polymers are also readily biodegraded by a wide range of aquatic and terrestrial microorganisms over reasonably short timeframes. Consequently, PHA-based biodegradable plastics are unlikely to accumulate in the environment.

In comparison, the biodegradation of PLA-based biodegradable plastics must be preceded by cleavage of ester bonds by oxidative or enzymatic hydrolysis reactions and microorganisms that

biodegrade PLA plastics are relatively scarce in the environment. The high temperature and humidity conditions obtained during industrial composting promote abiotic hydrolysis of PLA plastics and support thermophilic microorganisms that can biodegrade them. In comparison the degradation and biodegradation of PLA plastics in soil, sediment and water is very limited under normal environmental conditions with the result that PLA plastics will accumulate as litter within aquatic and terrestrial environments.

Oxo-degradable plastics degrade upon exposure to sunlight or heat whereupon they become brittle and fragment into smaller pieces of plastic and ultimately produce micro- and nano-plastic residues. Most assessments of the degradation and biodegradation of oxo-degradable PE plastics have been made after pre-treating them under accelerated and enhanced conditions (light and heat) that bear little or no resemblance to natural environmental conditions. Under natural environmental conditions the degradation of oxo-degradable PE plastics is significantly impaired and the timeframe for oxo-degradable plastics to degrade and fragment into smaller pieces is between 2 to 5 years.

Oxo-degradable plastics are not compostable as defined by international standards EN 13432 and ASTM 6400. Similarly, oxo-degradable PE plastics are biodegraded to a very limited extent in soil and water under natural environmental conditions. Oxo-degradable PE plastics should therefore not be labelled or marketed as being compostable or biodegradable.

Standards that assess the compostability and biodegradability of plastics and require 90% demonstrable degradation (EN13432, ISO 14855, ISO 16929, ASTM D6400) inadvertently allow for up to 10% of the original plastic to remain in compost or soil as plastic residues < 2mm size, or, microplastics (MPs). Such standards therefore inadvertently sanction the formation and accumulation of plastic and MP residues in compost and soil.

The fate and impact of plastic fragments and MPs produced by the degradation and fragmentation of oxo-degradable PE plastics during composting and within the wider environment remains unknown and is a concern. While no studies reporting negative impact of plastic fragments and MPs in soil were found, this was matched by a distinct absence of studies assessing their fate in soil and impact on terrestrial organisms, soil microbes, and soil function. Similarly, information on the fate and potential impact of sub-polymer units, oligomers and chemical additives released during the degradation and/or biodegradation of oxo-degradable and biodegradable plastics is relatively scarce.

A large number of chemical additives in some types of plastic are hazardous and known toxicants, and others can be degraded or transformed within plastic to biologically active and toxic chemicals. Despite the potential risk these additives present to the environment very few studies have investigated their migration and release from biodegradable plastics as they biodegrade, or from oxo-degradable plastics as they fragment, or their impact upon organisms exposed to them.

There is a need to develop and implement standards that assess the degradation and biodegradation of plastic either in the natural environmental or under conditions that are more representative of real environmental conditions, for extended periods of time, and in the absence of beneficial accelerating pre-treatments. Current methods for assessing the toxicity of by-products formed by the degradation of biodegradable and oxo-degradable plastics are inappropriate for assessing the wider range of chronic toxicity they can potentially exert upon organisms including endocrine disruption, mutagenicity, genotoxicity, or inflammatory responses. Modified standards that address

this current short coming are necessary to provide more realistic measures of the true extent of the degradability and biodegradability of plastics in the environment and their potential long-term environmental impact.

Emphasis should be placed on expanding the range of standards and tests for assessing the long-term impact of plastic residues and additive chemicals in high-value soils used to produce food. These new tests should include assessing changes to the physical and chemical properties of soil, and effects on soil organisms and microflora and fauna, soil microbial activity and function, and economically valuable food crops and plants.

Recommendations

In light of the information sources reviewed and summarised in this report the following recommendations are made to improve our knowledge of the biodegradation of biodegradable and oxo-degradable plastics, and ensure residues of these plastics have minimal or no long-term impact upon the environment

- PHA-type bio-based biodegradable plastics should be used in preference to PLA and oxo-degradable plastics for high-use high-volume plastic applications including single use plastic bags, waste and refuse bags, food packing and wrapping, and agricultural mulches.
- Oxo-degradable plastics should not be labelled as biodegradable or compostable.
- Any plastic product claiming to be compostable or biodegradable should be required to meet the minimum requirements of biodegradation in suitably robust standards (EN 13432, ISO 14855, ASTM D6400) and include a description of the conditions under which it was tested, duration of the test, and the extent of biodegradation that was achieved.
- Given its predominant use in single use plastic products and oxo-degradable plastics more research is required to identify the specific mechanisms by which microorganisms can degrade PE plastic so that PE plastics exhibiting improved biodegradation potential can be designed.
- Further research is required to assess the processes and timeframes in which oxo-degradable plastic fragments produce MPs, and their subsequent fate and impact in the environment.
- Further research is also required to determine if biodegradable PLA and oxo-degradable PE plastic residues can be biodegraded and mineralised in-situ in the environment and the timeframes in which this occurs.
- New standards that specifically assess the degradability and biodegradability of plastics under a range of natural environment conditions are required to obtain a true measure of the persistence and potential long-term impact of biodegradable and oxo-degradable plastics in the environment.
- Plastic manufacturers and industry representing bodies should be encouraged to make available information of the types and quantities of chemical additives used in the production of plastic products, including biodegradable and oxo-degradable plastics.
- New ecotoxicity tests that measure a wide range of multi-generational chronic toxicity endpoints are required to better assess and ensure the products formed by the degradation of oxo-degradable plastics do not adversely affect organisms exposed to them.
- There is an urgent need to rectify the absence of research on the impact of the degradation products and chemical additives released from biodegradable and oxo-degradable plastics in terrestrial ecosystems, and particularly high value soils used for the production of food.

This review has identified several significant gaps in our knowledge of the fate and potential impacts of residues of PLA-based biodegradable and oxo-degradable PE plastics in the environment. In light of these uncertainties it is pertinent to adopt a precautionary approach and exclude or limit the entry and use of these plastics in NZ until it can be demonstrated they have no long-term negative impact upon the environment.

1. INTRODUCTION

The American Society for Testing and Materials (ASTM) defines plastics as “a material that contains as an essential ingredient one of more organic polymer substances of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or processing into finished articles, can be shaped by flow” (ASTM D883-17).

A more common definition of plastic is a synthetic material made from a wide range of synthetic or semi-synthetic organic polymers (i.e. polyethylene, PVC, nylon, etc.) that can be moulded into shape while soft, and then set into a rigid or slightly elastic form. Plastics are organic polymers of high molecular mass, often contain other substances, and are typically synthetic and produced from petrochemicals. However, plastics can also be produced from different renewable materials such as starch, cellulose, polylactic acid (PLA) derived from corn starch, and polyhydroxyalkanoates (PHAs) produced by numerous microorganisms, including by the bacterial fermentation of sugar or lipids.

The low cost, advantageous properties and durability of plastics has resulted in a significant increase in the type and quantity of products manufactured from plastics in recent decades. However, the same properties and advantages that have made plastics the material of choice for so many different day-to-day products, combined with increasing usage, has created significant problems for their disposal, recycling and re-use - increasing pollution of the environment by plastics.

What is perhaps the single most popular property of plastics, their durability, has seen plastic residue become a significant worldwide environmental problem. Because of littering, inadequate or illegal waste disposal practices, accidental and unintentional discharge from land-based and aquatic activities, and unawareness on the part of consumers and the public, plastic has become a ubiquitous environmental pollutant.

The dramatic increase in the production combined with the resistance of commercial plastics to degradation, especially the type of plastics typically used in high-volume packaging, industry and agricultural applications, has focused the awareness of the public, regulators and the plastics industry, on the magnitude of the accumulation and impact of plastics in the environment.

The main types of polymers in single-use high-volume plastic items, typically polyolefins, are not designed to degrade in the environment, and the accumulation of parent plastic material and the microplastics they produce have become widely recognised as a significant threat to the health and wellbeing of our natural environment (Rochman et al, 2016; Peng et al, 2017).

Growing awareness of some of the environmental impact of plastics has increased demand for new generation plastics that provide improved re-use and recycling outcomes, that biodegrade completely in landfills or by composting, and/or can degrade and therefore have a significantly reduced or no long-term impact within receiving environments.

The plastic industry has suggested that degradable and biodegradable plastics have an important role to play in reducing the volume of plastic waste and its accumulation and impact in the environment. However, there is a lot of confusion regarding the advantages and disadvantages of degradable and biodegradable plastics, how the public interpret the specific terms used to describe them, and their ultimate impact within the environment.

To address these issues the Parliamentary Commissioner for the Environment (PCE) has undertaken a program of work investigating the merits of biodegradable and compostable plastics. As part of this work program PCE commissioned Northcott Research Consultants Limited (NRC Ltd) to review the current literature and produce a report on biodegradable plastics. The following sections of this report:

- outline the descriptions and definitions commonly used to describe plastics and biodegradable plastics
- summarise standard methods to assess the biodegradation of plastics
- define the major classes of biodegradable plastics and specifically
- discuss the chemical composition of biodegradable PHA and PLA based plastics and oxo-degradable degradable plastics
- describe the processes by which biodegradable plastics degrade, the chemicals they are transformed into, and chemical additives they can release
- describe standard methods used to assess the toxicity of residual materials produced by the biodegradation of biodegradable and oxo-degradable plastics
- discuss alternative ecotoxicity approaches for assessing a wider range of potential impacts resulting from the biodegradation of biodegradable and oxo-degradable plastics

2. DEFINITIONS OF DEGRADABLE AND BIODEGRADABLE PLASTICS

It is accepted that degradable and biodegradable plastics have an important role to play in reducing the volume of plastic waste and its accumulation and impact in the environment. However, there is much confusion regarding the advantages and disadvantages of degradable and biodegradable plastics, how the public interprets the specific terms used to describe them, and their ultimate impact within the environment.

There is considerable debate about the extent to which plastics, including degradable and biodegradable plastics, really do degrade in the environment. This debate occurs in the scientific literature between polymer scientists producing modified or new degradable plastics, and environmental scientists assessing the degradability of plastics under natural environmental conditions. The most intense level of debate occurs between organisations manufacturing different types of plastics, the producers of additive chemicals that promote the degradation of plastics, and the waste management and recycling sectors (UNEP, 2015). Consequently, there is considerable confusion regarding the terminology used to describe plastic and its degradability and behaviour in the environment.

The terms commonly used to describe plastics and polymers can be confusing to those not wholly familiar with their meaning as some synthetic polymers are produced from non-renewable fossil fuels, some from bio-based renewable sources, and some from both (figure 1). Some polymers produced from non-renewable fossil fuel can be biodegradable while other polymers produced from bio-based renewable sources may be non-biodegradable.

Within this report the following definitions have been used to avoid confusion regarding different types of plastics, their properties, and specific processes being discussed.

Plastic describes a synthetic material made from a wide range of synthetic or semi-synthetic organic polymers (i.e. polyethylene, PVC, nylon, etc.) or natural biopolymers that can be moulded into shape while soft, and then set into a rigid or slightly elastic form. Plastics are typically organic polymers of high molecular mass and often contain other substances.

Polymers are large molecules, or macromolecules, composed of many repeated subunits, and can be synthetic or natural.

Because of their broad and often unique range of properties both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers include synthetic plastics such as polyethylene and natural biopolymers like lignin and proteins. Whether they are natural or synthetic, polymers are created by the polymerisation of many small molecules, known as monomers. Their subsequent large molecular mass relative to small molecule compounds produces unique physical properties, including toughness and durability, and elasticity.

2.1 Degradable versus biodegradable

Any material, including plastic, can be described as degradable or biodegradable if it meets specific criteria described within an appropriate testing standard. The degradation of plastic occurs over

time and is dependent upon the properties of the plastic polymer, environmental conditions, and the presence of microorganisms.

Plastics New Zealand (the Industry association representing plastics companies across NZ) has adopted the definitions of bioplastics and biodegradable plastics used by European Bioplastics (the association representing the interests of the European bioplastics industry) which is based on differentiating the source of primary material from which biodegradable plastics are produced (figure 1).

Bioplastics include many different materials with differing properties and applications. A plastic material is defined as a bioplastic if it is either bio-based, biodegradable, or both.

Bio-based means that the plastic material or product is at least partly derived from biomass, or plant-based material, for example from corn, sugarcane or cellulose.

It is important to recognise that a bio-based material or plastic product manufactured from a bio-based material may not be biodegradable.

Bioplastics are differentiated into three main classes, these being:

Bio-based or partly bio-based, non-degradable plastics including the polyolefins polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) can be made from renewable resources like bioethanol. Others are partially bio-based and include polyethylene terephthalate (PET, otherwise known as polyester when used to produce synthetic textiles), the polyester polytrimethylene terephthalate (PTT), and thermoplastic polyester elastomers (TPC-ET).

Biodegradable and bio-based plastics are produced fully or partly from renewable biomass (material of biological origin) and not from fossil fuels. These plastic products are designed to be composted in industrial composting facilities under specified operating conditions and are biodegradable. With the exception of pure PLA they can be composted in home composting systems. The most common types of biodegradable bio-based plastics are derived from polylactic acid (PLA), polyhydroxyalkanoates (PHA) including polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and polyhydroxybutyrate-co-hydroxyvalerate blends (PHBV), polybutylene succinate (PBS), and starch blends.

Biodegradable and fossil-fuel based plastics are produced from fossil fuel sources and include polybutylene adipate terephthalate (PBAT) and polycaprolactone (PCL) which can biodegrade and domestically and industrially composted.

2.2 Oxo-degradable plastics

Oxo-degradable plastics are a specific type of degradable plastic composed of traditional fossil fuel-based plastics (usually PE or PP) incorporating specific additives that accelerate their degradation. These additives are often referred to as prodegradants or oxo-additives, and are typically transition metal (Fe, Ni, Co or Mn) salts of carboxylic acids and dithiocarbamates (Wiles, 2005a). The plastics that contain prodegradants are called oxo-degradable plastics or oxo-plastics. The prodegradants within the polymeric structure initiate the breakdown of the normally stable long molecular chains

which results in the polymer becoming brittle and fragmenting into smaller sized pieces. Depending upon the properties of the prodegradant(s) the breakdown of oxo-degradable plastics is initiated either by heat, exposure to UV light, or a combination of both. Most oxo-degradable plastics are produced from fossil fuel-derived polymers that are commonly used to manufacture high production volume plastics, for example polyethylene (PE) and polypropylene (PP). The main uses of oxo-degradable plastics include high-volume single-use applications such as single-use plastic bags, refuse and compost sacks, food and clothes packaging, and agricultural mulch films.

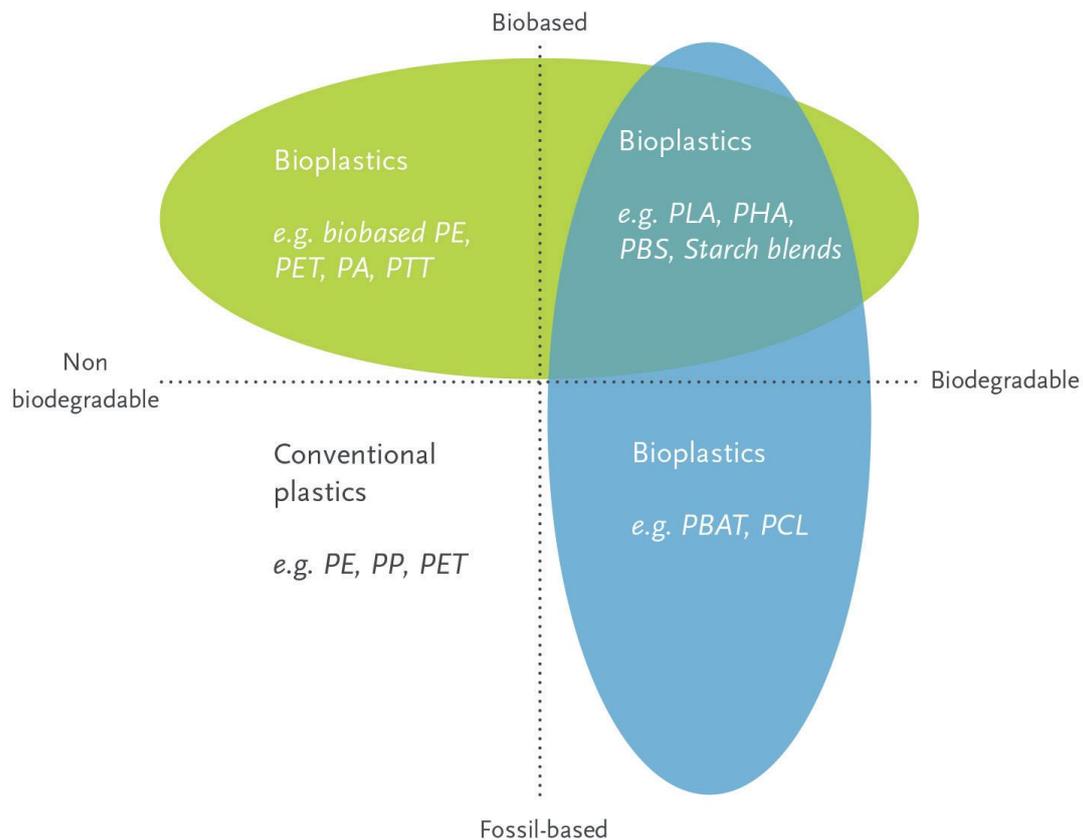


Figure 1: diagrammatic representation of the differentiation and definition of biodegradable plastics (source: European Bioplastics)

While oxo-degradable plastics and biodegradable bio-based blends of plastic are often described as being degradable, they contain fossil fuel-based components and are not compostable nor fully biodegradable. These types of plastics require specific conditions to initiate the degradation process, for example exposure to heat, sunlight and air.

Regardless, the number of plastic materials and products produced and marketed as being ‘oxo-degradable’ or ‘oxo-biodegradable’ is increasing and manufacturers continue to make claims their products provide improved environmental outcomes.

However, the main effect of oxidation, or oxo-degradation, is the fragmentation of the parent plastic into small particles that persist and accumulate within the environment. These products do not

comply with standards for compostability, are not considered bioplastics, and do not meet the requirements of biodegradability as specified within accepted industry standards (see Part 3).

2.3 Definitions of plastic degradability

The degradability or biodegradability of plastic polymers is dependent upon the composition of the polymer and the environmental conditions it is exposed to. The terms used to describe the degradability of plastic polymers, particularly those used by producers to market their products, are often insufficiently described, leading to confusion and/or misunderstanding by consumers. Many plastics claiming to be biodegradable are instead bioerodable, hydrobiodegradable, photodegradable, or only partially biodegradable.

Degradation is the process in which an organic compound is transformed into simpler compounds. With respect to plastics, degradation represents a change in the chemical structure that produces a significant reduction of its properties including changes in flexibility, tensile strength, dielectric properties, and surface area. The processes by which this occurs includes thermal (heat), photolytic (light), oxidative (reaction with oxygen) and hydrolytic (reaction with water) degradation, and biodegradation (microbial degradation). All plastics, including biodegradable plastics, can be degraded by abiotic chemical processes.

As plastics degrade with time the resulting physical changes ultimately leads to the structure of the plastic beginning to physically disintegrate or breakdown into small fragments. These smaller fragments of plastic are more susceptible to chemical and microbial degradation with the result that the polymeric structure of the plastic fragments itself starts to degrade into smaller polymeric units. The degrading of the core polymer structure into smaller size polymeric units produces polymer sub-units of reduced molecular mass and is evidenced by changes in the molecular weight distribution from that of the parent polymer.

Biodegradation is degradation by biological processes brought about by the action of naturally occurring microorganisms (bacteria, fungi and algae). Biodegradability as defined by the European Standard EN 13432 is the breakdown of an organic compound by micro-organisms in the presence of oxygen to carbon dioxide, water, mineral salts and new biomass, or in the absence of oxygen, to carbon dioxide, methane, mineral salts and biomass. Plastics that are truly biodegradable will break down and be degraded by microorganisms into these ultimate end products. The degradation of organic materials into these final benign end products (carbon dioxide, water or methane, mineral salts and biomass) is correctly defined as mineralisation. Mineralisation represents the ultimate measure and endpoint for biodegradable plastics.

Composting describes a managed process involving the biological decomposition and transformation of biodegradable material to produce carbon dioxide, water, minerals and organic matter in the form of compost or humus.

Compostable plastics are another specific type of degradable plastic and are defined by a number of internationally recognised standards (EN 13432, ASTM D 6400) as “a plastic that undergoes

degradation by biological processes during composting to yield CO₂, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leaves no visible, distinguishable or toxic waste". To be industrially compostable, a plastic must biodegrade under defined conditions prior to a specific endpoint within a period of 180 days. Furthermore, standards EN 13432 and ASTM D6400 specify four basic provisions that govern how a compostable plastic must perform in a simulated compost environment, these being:

1. the product must be demonstrated to contain an acceptable concentration of residual metals and acceptable levels of volatile/degradable material.
2. the product must actually biodegrade (i.e. be consumed by microorganisms) at a rate comparable to a known compostable reference material (cellulose for example).
3. the product must physically disintegrate to the extent that it cannot be "readily distinguishable" from the finished compost product (humus).
4. the product cannot have adverse impacts on the ability of the compost to support plant growth (it cannot be phytotoxic)

It is important to realise that a plastic product designed to biodegrade may not necessarily meet the requirements of compostability as defined in these internationally recognised standards. Biodegradable plastic products are designed to biodegrade in specific environments, for example the marine environment, in soil, or within anaerobic landfills, while others are intended to biodegrade and be properly managed within industrial compost facilities.

Degradation of plastics is a chemical process that alters its chemical structure and changes its physical properties.

Biodegradation is degradation by biological processes from the action of natural microorganisms.

Composting is a managed process that biologically decomposes and transforms biodegradable material to carbon dioxide, water, minerals and organic matter.

Biodegradable and bio-based plastics are manufactured fully or partly from renewable biomass, are designed to be composted in industrial composting operations under specific conditions, and are biodegradable.

Oxo-degradable plastics are made of fossil fuel based plastics and contain prodegradants that enhance their chemical degradation. They are not compostable or fully biodegradable.

Compostable plastics are a specific type of degradable plastic that degrades by biological processes as defined by internationally recognised standards.

3. TESTS AND STANDARDS FOR ASSESSING THE DEGRADABILITY AND BIODEGRADABILITY OF PLASTICS

Various internationally recognised organisations including the American Society for Testing and Materials (ASTM), European Committee for Standardisation (CEN or EN), and International Organisation for Standardisation (ISO) have established standards and testing methods to assess the biodegradability and compostability of plastics. ISO is an internationally recognised standardisation body whereas ASTM and CEN are significant regional standardisation bodies. Additionally, there are several national standardisation bodies including the Austrian Standard Institute (ONORM), the British Standards Institute (BSI), the German Deutsches Institut für Normung (DIN), the French Association Française de Normalisation (AFNOR), the Italian Ente Nazionale Italiano di Unificazione (UNI) and the Japanese Biodegradable Plastics Society (BPS) (Krzan et al, 2006).

These organisations continue to improve and update the feasibility and reproducibility of standard laboratory methods to assess the degradation and biodegradation of plastics. These standards provide a basis to test and validate the increasing number of plastic products that are designed to provide improved environmental outcomes by being biodegradable or oxo-degradable. These standards provide consistency, accountability and reliability to the results and the tested product, and establish the basic requirements, specifications, and criteria for subsequent certification and labelling of biodegradable or oxo-degradable products.

3.1 Standards for assessing the compostability of plastics

In response to the widespread use of plastic bags to collect and store refuse, and importance of composting to reduce municipal waste and produce a publicly acceptable re-useable product, numerous standards have been specifically developed to assess the aerobic biodegradation and degradation of plastics under composting conditions. These standards range from those that merely assess the disintegration of plastic products, through to those assessing aerobic and/or anaerobic biodegradation, and biodegradation under more extreme thermophilic conditions. Due to the significance of composting to manage municipal waste these later standards typically produce more robust and reliable data than those assessing the degradation and biodegradation of plastic in other media such as water and soil.

A selection of primary standards provided by ISO, CEN and ASTM for assessing the compostability of plastics, including biodegradable plastics, is listed in Table 1. This is by no means a complete list. ISO committee T61/SC5/WG22 has issued 23 active standards for assessing the degradation and biodegradation of organic compounds and plastics that are relevant for assessing the biodegradability of biodegradable and oxo-degradable plastics. Similarly, ASTM has 26, and CEN has twelve relevant standards. These organisations continually review and modify existing standards, and issue new and improved ones.

To demonstrate the range and sometimes subtle differences that can exist between the standards produced by these organisations, a selection of standards developed by ASTM to determine the degradation and biodegradation of plastics are listed in Table 2.

Most of these standards specify requirements for assessing biodegradability and this reflects the unanimous opinion of scientists that biodegradation is the only sure means by which plastics will be ultimately degraded. While the system requirements, complexity, and capability between the biodegradability standards is varied they all assess the biodegradation process by measuring either the evolution of carbon dioxide, consumption of biological or chemical oxygen demand, or reduction of dissolved organic carbon.

Standards developed to assess the biodegradation of plastics through the evolution of carbon dioxide or consumption of oxygen are subject to various operational difficulties, particularly those conducted under solid-state conditions and in the presence of organic rich media like soil and/or mature compost. In comparison, degradation and biodegradation tests carried out in aqueous media are generally less complex to set up and provide higher levels of reproducibility due to their intrinsic higher level of homogeneity. The rate and extent of biodegradation of plastics under solid-state conditions can be affected significantly by inherently variable parameters like the composition and activity of microbial inoculum, and procedural parameters including the concentration of test material in the solid media, duration of the test, and the reference material used in a standard test.

Each standard for assessing the biodegradability of plastics recommends the application of specific analytical techniques and testing conditions that are suitable for determining one of three types of biodegradability, these being: *ready*, *inherent*, and *ultimate* biodegradability (Krzan et al, 2006). It's crucial to understand the differences between these terms to select an appropriate standard to test the biodegradability of a plastic, and to subsequently interpret the test results.

A *readily biodegradable* substance or material is rapidly and completely mineralised in a short period of time after being exposed to the most common environment. Examples include the OECD 301-D closed-bottle and OECD 301-A die-away tests (OEC, 1992). A positive result from these tests indicates the substance or material can readily degrade in the natural environment.

An *inherently biodegradable* substance or material is one that biodegrades to a specified endpoint (%) within a specified time under the most favourable environment. Examples of this test include the OECD 302A Modified semi-continuous activated-sludge (SCAS) test (OECD, 1981). A positive result from this test indicates that although the degradation process will be slow the substance or material can degrade and will not persist in the environment.

An *ultimately biodegradable* substance or material is one that biodegrades under defined conditions that simulate those within a specific environment, for example under composting, in a landfill, in agricultural soil. The most common test methods measure the evolution of carbon dioxide and a positive result indicates the substance or material is biodegraded in the environment under similar testing conditions, to the extent that all biological, toxicological, chemical and physical properties of the material are eliminated.

Table 1: Examples of standards for assessing the degradability and/or biodegradability of plastics under composting conditions

Standard ID	Organisation	Description	Purpose
EN 13432	CEN ^A	Packaging - Requirements for packaging recoverable through composting and biodegradation - Test scheme and evaluation criteria for the final acceptance of packaging.	Determines the compostability and anaerobic treatability of packaging and packaging materials by addressing biodegradability, disintegration during biological treatment, effect on the biological treatment process, effect on the quality of the resulting compost.
EN 14995	CEN ^A	Plastics - Evaluation of compostability - Test scheme and specifications.	Specifies requirements and procedures to determine the compostability or anaerobic treatability of plastic materials by addressing four characteristics: I) biodegradability, II) disintegration during biological treatment, III) effect on the biological treatment process and IV) effect on the quality of the resulting compost.
EN/ISO 20200	CEN ^A /ISO ^B	Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test.	Determines the degree of disintegration of plastic materials in a pilot-scale aerobic composting test under defined laboratory conditions.
EN 14045		Packaging - Evaluation of the disintegration of packaging materials in practical oriented tests under defined composting conditions.	Packaging materials are mixed with biowaste and spontaneously composted for 12 weeks in practical oriented composting conditions.
ISO 16929	ISO ^B	Plastics - Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test.	Determines the degree of disintegration of plastic materials in a pilot-scale aerobic composting test under defined conditions.
EN 14046	CEN ^A	Packaging - Evaluation of the ultimate aerobic biodegradability of packaging materials under controlled composting conditions - Method by analysis of released carbon dioxide.	Evaluates the ultimate aerobic biodegradability of packaging materials based on organic compounds under controlled composting conditions by measurement of released carbon dioxide at the end of the test.
EN/ISO 14855-1	CEN ^A , ISO ^B ,	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide - Part 1: General method.	Determines the ultimate aerobic biodegradability of plastics, based on organic compounds, under controlled composting conditions by measurement of the amount of carbon dioxide evolved and the degree of disintegration of the plastic at the end of the test. The test method is designed to yield the percentage conversion of the carbon in the test material to evolved carbon dioxide as well as the rate of conversion.

^A CEN = European Committee for Standardisation; ^B ISO = International Organization for Standardization, ^C ASTM = American Society of Testing and Materials

Table 1: Examples of standards for assessing the degradability and/or biodegradability of plastics under composting conditions- continued

Standard ID	Organisation	Description	Purpose
EN/ISO 14855-2	CEN ^A , ISO ^B ,	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide - Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test.	Determines the ultimate aerobic biodegradability of plastic materials under controlled composting conditions by gravimetric measurement of the amount of carbon dioxide evolved. The method is designed to yield an optimum rate of biodegradation by adjusting the humidity, aeration and temperature of the composting vessel.
ASTM D6400 - 12	ASTM ^C	Standard specification for labelling of plastics designed to be aerobically composted in municipal or industrial facilities.	Determines if plastics and products made from plastics will compost satisfactorily, including biodegrading at a rate comparable to known compostable materials. To establish standards for identifying products and materials that will compost satisfactorily in commercial and municipal composting facilities.
ASTM D5338 - 15	ASTM ^C	Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures.	Determines the degree and rate of aerobic biodegradation of plastic materials on exposure to a controlled-composting environment under carefully controlled laboratory conditions, at thermophilic temperatures. This test method operates under controlled conditions resembling composting, where thermophilic temperatures are achieved. Test substances are exposed to an inoculum obtained from compost produced from municipal solid waste.
ASTM D6868 - 17	ASTM ^C	Standard specification for labelling of end items that incorporate plastics and polymers as coatings or additives with paper and other substrates designed to be aerobically composted in municipal or industrial facilities.	Determine if end items (including packaging) which use plastics and polymers as coatings or binders will compost satisfactorily, in large scale aerobic municipal or industrial composting where maximum throughput is a high priority and where intermediate stages of plastic biodegradation should not be visible to the end user for aesthetic reasons.

^A CEN = European Committee for Standardisation; ^B ISO = International Organization for Standardization, ^C ASTM = American Society of Testing and Materials

Table 2: Examples of ASTM standards for assessing the degradability and/or biodegradability of plastics

Standard designation	Purpose of standard	Description
ASTM D6954 - 18	Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation.	Compares and ranks controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal and photo-oxidation processes as well as the biodegradation and ecological impacts in defined applications and disposal environments after degradation.
ASTM D5988 - 18	Standard test method for determining aerobic biodegradation of plastic materials in soil.	Determines under laboratory conditions the degree and rate of aerobic biodegradation of plastic materials, including formulation additives, in contact with soil.
ASTM D5526 - 12	Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions.	Determines the anaerobic biodegradability of plastic products when placed in biologically active environments simulating landfill conditions.
ASTM D7475 - 11	Standard test method for determining the aerobic degradation and anaerobic biodegradation of plastic materials under accelerated bioreactor landfill conditions.	Determines the degree and rate of aerobic degradation (as indicated by loss of tensile strength, molecular weight, possibly resulting in disintegration and fragmentation) and anaerobic biodegradation of plastic materials in an accelerated bioreactor landfill test environment.
ASTM D6691 - 17	Standard test method for determining aerobic biodegradation of plastic materials in the marine environment by a defined microbial consortium or natural sea water Inoculum.	Determines the degree and rate of aerobic biodegradation of plastic materials exposed to pre-grown marine microorganisms under controlled laboratory conditions.
ASTM D5511 - 18	Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic-digestion conditions.	Determines the degree and rate of anaerobic biodegradation of plastic materials in high-solids anaerobic conditions where they are exposed to a methanogenic inoculum derived from anaerobic digesters operating only on pre-treated household waste.
ASTM D7444 - 11	Standard practice for heat and humidity aging of oxidatively degradable plastics.	Tests the oxidative degradation characteristics of plastics that degrade in the environment under atmospheric pressure and thermal and humidity simulations only.
ASTM WK41850	New Test Method for Determining the rate and extent of plastics biodegradation in an anaerobic laboratory environment under accelerated conditions.	This new standard which is under development is a laboratory assessment of the extent and rate of biodegradation of plastics in a simulated landfill environment.

Standards for biodegradability testing can be further classified into three groups: preliminary, simulated, and complimentary tests. A full discussion of this classification with reference to specific standards of biodegradability is provided by Krzan (Krzan et al, 2006). Preliminary standard tests determine “*ready*” biodegradability and are typically completed as part of an initial screening assessment. These preliminary tests are carried out under simplified environmental conditions, typically aqueous or soil media, and the results indicate the tested material can readily degrade in most natural environments.

Simulated, or accelerated test procedures provide a more comprehensive assessment of the degradation process, for example, determining the rate of degradation and/or the formation and concentration of transformation products. Simulated tests are typically carried out using lower concentrations of material in a targeted environment (composting, landfill, aquatic marine) requiring specialist measurement techniques and specific preparation procedures. The results of these standard tests demonstrate the *ultimate* biodegradability of the test material in a targeted environment under specific conditions, and as such they are widely applied for assessing the biodegradability and certification of biodegradable plastics.

Complimentary tests are typically carried out to obtain supplementary data on test materials, for example their biodegradability under anaerobic conditions and for determining *inherent* biodegradability. These tests typically employ conditions selected to produce the highest or most favourable degradation outcomes. Results from these types of biodegradability tests must therefore be treated with caution when being interpreted and/or subsequently applied to estimate the biodegradability of plastics in real-world environments.

This last point is particularly relevant to those standards assessing the biodegradation of plastics under composting conditions. A critical point regarding standards assessing the degradability and biodegradability of plastics under composting is that they are conducted under highly defined conditions including temperature and biological activity, and the testing time scales are optimised for the biodegradation of plastics. These standards require specific measured endpoints to be met before a plastic can be classified as compostable. Significantly, this does not mean a plastic must be totally (100%) biodegraded. For example, standard ASTM D6400 requires >90% of the CO₂ that can be theoretically evolved from a biodegrading plastic is achieved within 180 days, but allows residues of plastic <2mm in size, or microplastics (MPs), to remain in the final compost. The requirement that 90% of the carbon in the original tested product is recovered from the biodegradation process as CO₂ accepts a ±10 per cent statistical variability in the experimentally determined measurement. Hence there is an expectation that complete biodegradation will be achieved. However, theoretically it is possible for up to 10% of the original biodegradable or oxo-degradable plastic to remain in a final compost as plastic residue <2mm in size, which classifies them as microplastics.

The ISO, CEN and ASTM standards for assessing the biodegradation of plastics during composting are predominantly controlled laboratory-based tests that maintain optimal conditions for biodegradation, sometimes but not always including a thermophilic phase, for relatively prolonged periods of time (up to 180 days and sometime beyond). While the outcomes of such laboratory tests are often conservative they should not be considered a substitute for assessing the biodegradability of plastics in operational compost plants that are subject to the influence of external factors that are

difficult to control. Reflecting on this, European Bioplastics, the organisation representing European bioplastics industries, states “the limits and duration of biodegradation defined for, and derived from laboratory testing, should not be applied to full scale composting plants”. Instead they recommend full-scale testing should be carried out at a specific plant with a specific composting technology to confirm a plastic material meets the biodegradation requirements specified in European standard EN 13432 under real composting plant operating conditions (European Bioplastics. 2015a).

The conditions specified in ISO, CEN and ASTM standards for the biodegradation of plastics under industrial composting processes are achievable within modern well run industrial and municipal composting facilities. However, it is impossible to maintain these specified temperatures for the required length of time in domestic home composting systems with the outcome that many “biodegradable” plastics are not broken down at all and remain intact after domestic composting. Most consumers are not aware or informed of the significant differences that exist between commercial and home composting systems and assume compostable plastics they purchase will fully biodegrade in their home compost system.

An unintended consequence of the availability of the numerous different standards for assessing the biodegradability of plastics is that it provides plastic manufacturers the opportunity to select and implement a testing standard to inflate their claims of product biodegradability. For example, some manufacturers asserting their degradable plastic refuse bags anaerobically degrade within landfills have assessed their biodegradation using standard ASTM D7475-11. As specifically stated in ASTM D7475-11 this test method does not simulate all conditions found in landfills, especially those within biologically inert landfills. Instead the method is designed to simulate conditions in highly managed active bioreactor landfill operations where methane gas is recovered, and/or its generation is actively promoted by inoculation, moisture and temperature control, the injection of oxygen, or heating and recirculation of leachate. Assessing the biodegradation of degradable plastics by this test method will provide a higher rate and extent of anaerobic biodegradation than could ever be achieved for degradable plastic refuse bags within most full-scale landfills.

It is misleading for a manufacturer or distributor to claim a plastic product is biodegradable without providing confirmatory information about the standard specification that was applied to determine biodegradability. If a material or product is advertised as biodegradable, further information about the timeframe, the level of biodegradation achieved, and the required environmental conditions should be provided via appropriate labelling, so it is readily available to consumers.

One of the most important issues concerning the environmental impact of biodegradable plastics is the extent to which they biodegrade. The rate and extent to which they biodegrade in receiving environments is dependent upon the chemical composition of the biodegradable polymer, the additives it contains, and the real-world environmental factors it is subject to. Consequently, there is increasing demand from consumers and regulators for new standards that assess the biodegradability of plastics under the “real world” conditions encountered in terrestrial and aquatic environments. New standards are required to address the uncertainties regarding the impacts resulting from the long-term accumulation and slow rate of biodegradation of plastic residues in the

environment. Such standards, in combination with improved labelling, will enable consumers to make better informed purchase decisions that can lead to improved environmental outcomes.

Various internationally recognised standards have been developed to assess the biodegradability and compostability of plastics.

There are significant differences between the conditions maintained in industrial and home composting processes and industrial composting is a significantly more robust and efficient process.

Many biodegradable plastic products are not broken down and degraded by home composting.

Manufacturers of plastic products advertised as being biodegradable should provide information on the timeframe in which the level of biodegradation is achieved and the necessary environmental conditions required on product labels.

There is a need for new standards that assess the biodegradability of plastics under real world environmental conditions.

4. TYPES AND USES OF DEGRADABLE AND BIODEGRADABLE PLASTICS

4.1 Biodegradable plastics

The most common types of biodegradable plastics polyesters include polylactate or polylactic acid (PLA), poly(3-hydroxybutyrate) (PHB), poly(propiolactone) (PPL), poly(4-hydroxybutyrate) (P4HB), polycaprolactone (PCL), poly(ethylene succinate) (PES), poly(butylene succinate) (PBS), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV) and poly(ester carbonate) (PEC) plastics. The structures of the base monomers making up the polymeric structures of these biodegradable plastics are shown below in figure 2. PHB, P(4HB) and PHBV are individual chemicals within the wider class of polyhydroxyalkanoate (PHA) chemicals produced by bacteria that are used to produce PHA biodegradable plastics.

Examples of various biodegradable polymers produced from bio-based renewable feedstock and fossil fuel sources together with the trade names of commercially available sources are listed in Table 3.

Due to their key properties of biodegradability, biocompatibility and manufacture from renewable resources and its application in biodegradable medical implants PLA is the most widely used bio-based and biodegradable plastic. The most common uses of higher production volume biodegradable PLA and PHA-type plastics are in high-use packaging materials and waste collection bags. Other uses include catering products, food wrappings and films, food containers, egg cartons, laminated paper, hygiene products, biomedical applications, disposable nappies, plastic shopping bags, and there is increasing uptake of their use in agriculture (plastic weed mulch, hay and silage wrapping etc.) (Table 4).The recent announcement of the opening of the first commercial PHA production plant in the USA in 2019 is expected to result in a considerable increase in the production of PHA biodegradable plastic material for a wide variety of applications including biodegradable food packaging and drinking straws.

4.2 Oxo-degradable plastics

Oxo-degradable plastics are typically used as high-volume plastic films in a range of products for agriculture, packaging and waste disposal applications such as refuse and composting sacks. In agriculture oxo-plastics are used as mulching films for growing vegetables and fruit, providing a controlled environment for conserving water and/or barrier protection against frost damage. Other agricultural uses include hay and silage wrap, grow bags, and sometimes plant pots made of polystyrene. Other major uses of oxo-degradable plastics are as single use plastic carrier bags and other types of plastic bags used to package food or clothes (Wiles, 2005a), and bread bags, shrink film, bubble wrap, bottles and cups (Deconinck and De Wilde, 2013).

Some of the international companies producing oxo-degradable plastics and products are Add-X Biotech (Addiflex®), EPI Environmental Technologies (TDPA®), EcoPoly Solutions (EcoPoly®), Symphony Environmental Technologies (d₂w® additive), Wells Plastic (Reverte®), and Willow Ridge Plastics (PDQ-M, PDQ-H, BDA and OxoTerra™).

Biodegradable plastics are principally used in high-use high-volume commodity products and have particular application as food packaging, compost and rubbish bags, wrapping films and paper coatings.

Oxo-degradable plastics are used in single use plastic carrier bags, rubbish bags and compost sacks, packaging, and in agriculture as plastic mulch, hay and silage wrap, and grow bags.

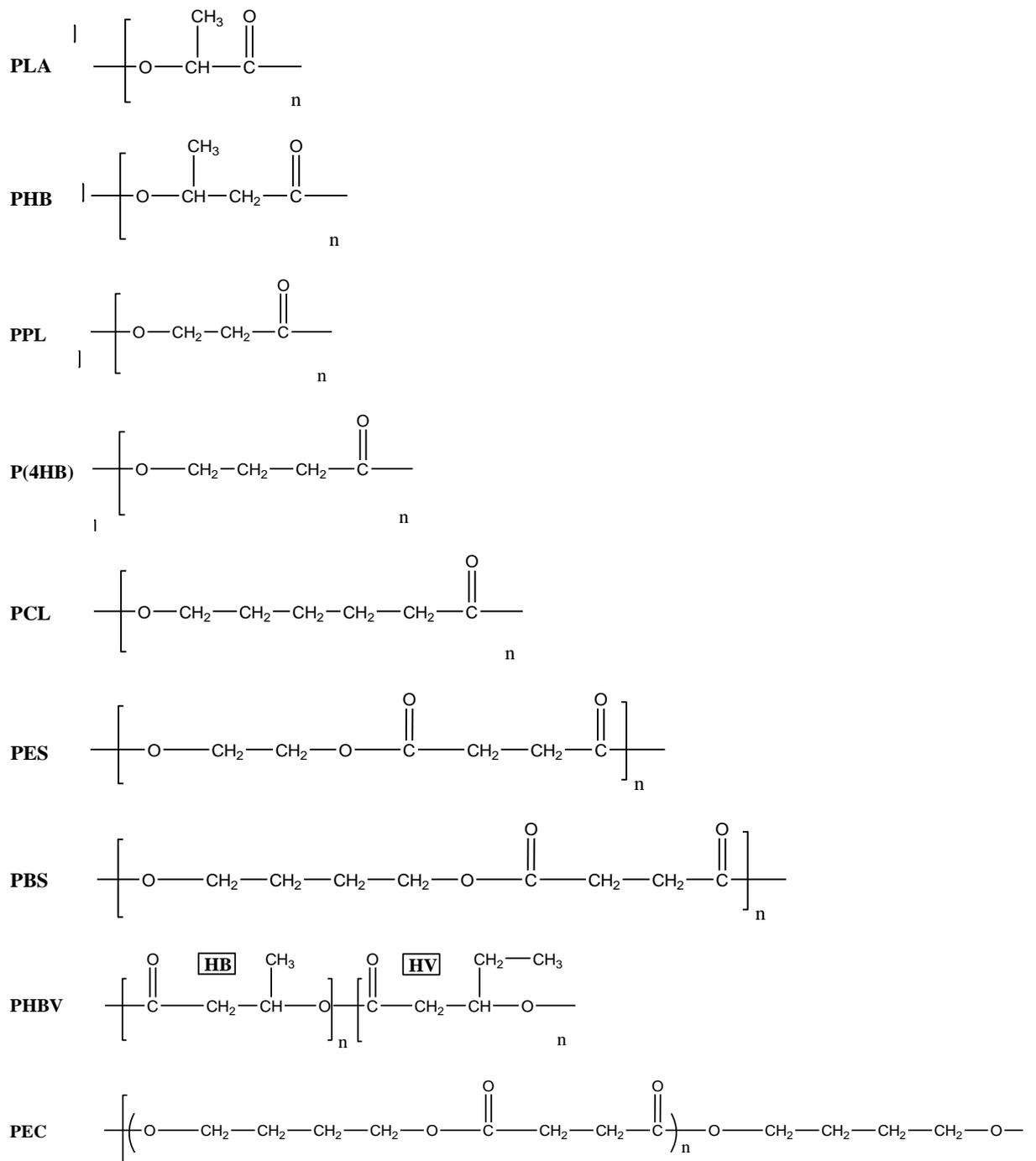


Figure 2 Chemical structures of the monomers in biodegradable plastics PLA, PHB, poly(propiolactone) (PPL), poly(4-hydroxybutyrate) (P(4HB)), polycaprolactone (PCL), poly(ethylene succinate) (PES), PBS, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(ester carbonate) (PEC). PHB, P(4HB) and PHBV are all classed as polyhydroxyalkanoates (PHAs). Source: Tokiwa and Calabia 2004.

Table 3: Biodegradable polymers from renewable and fossil fuel sources (Rudnik 2008).

Polymers from renewable sources	Primary feedstock/sources	Trade names
PLA polylactide	Lactic acid by chemical synthesis or carbohydrate fermentation	Lacea, Lacty, Nature works, Hycail
PBS poly(butylene succinate)	Synthetic polyester made by polycondensation with raw materials from renewable feed stock	BioPBS™
PHA poly(hydroxyalkanoates)	Synthesised by bacteria (carbohydrates, alkanes, organic acids etc.)	Biopol®, AONILEX®, Nodax®
PHB poly(hydroxybutyrate)		
PHV poly(hydroxyvalerate)		
PHBV poly(3-hydroxybutyrate-co-3hydroxyvalerate)		
PHBH poly(hydroxybutyrate-co-hydroxyhexanoate)		
		PHBH™
TPS thermoplastic starch	Starch	Solanyl, BioplastTPS, Evercorn, Plantic, Biopar, Placorn
Cellulose	Esterification of cellulose (wood, cotton, hemp, sugar cane, corn etc.)	Natureflex, Tenite, Bioceta, Cellidor
CA cellulose acetate		
CAP cellulose propionate		
CAB cellulose acetate butyrate		
Chitosan	De-acetylation of chitan from shells of shellfish and seafood processing waste	Chitosan
Polymers from Fossil fuel sources	Primary feedstock/sources	Trade names
Aliphatic polyesters and copolyesters	Synthetic polyesters made by polycondensation with raw materials from petrochemical feed stock	Bionolle®, Skygreen
PBS poly(butylene succinate)		
PBSA poly(butylene succinate adipate)		
PES poly(ethylene succinate)		
PESA poly(ethylene succinate adipate)		
PCL poly(caprolactone)	Linear polyester produced by ring opening polymerisation of a ϵ -caprolactone	Tone, CAPA, Placel
PEA poly(esteramide)	Polycondensation of α -amino acids, aliphatic dicarboxylic acids, and diols	BAK
PVA poly(vinylalcohol)	Polymeriation of vinyl acetate	Mowiol, Erkol, Sloviol, Polyvinol, Elvanol
Aromatic copolyesters	Polycondensation with raw materials from petrochemical feed Stock	Biomax®, Eastar Bio®, Sorona Ecoflex® Corterra®, Permastat
PBST poly(butylene succinate terephthalate)		
PBAT poly(butylene adipate terephthalate)		
PTT poly(trimethylene terephthalate)		

Table 4: Uses for PLA and PHA-type biodegradable plastics

Plastic	Uses
Biodegradable plastics	
Polylactic acid (PLA)	Packaging and paper coatings, drink cups, cutlery, food trays, mulch films, compost bags, planter boxes
Polyhydroxybutyrate (PHB)	Bottles, bags, wrapping films, compostable bags, and potting containers, disposable nappies
Polyhydroxyvalerate (PHBV)	Films and paper coatings

(Sourced from Scott,2005; Shah et al, 2008)

5. THE DEGRADATION OF PLASTICS

All types of plastics are subject to degradation but the extent to which they degrade depends on the properties of the polymer itself, the chemical additives they contain, the environmental conditions to which they are exposed, and time. The degradation of plastics resulting from environmental factors including light, heat moisture chemical conditions or biological activity is evidenced by physical and chemical changes of their polymeric structure and material properties (mechanical, optical or electrical). Degradation typically produces cracking, erosion, pitting, delamination and discolouration of plastics. At the molecular level the changes include the breaking of chemical bonds, and the transformation and formation of chemical groups, most often involving the incorporation of oxygen (oxidation).

The degradation of plastics is ultimately achieved through a combination of physical, chemical and biological processes. These can be grouped into three broad processes: fragmentation, degradation, and biodegradation, and include:

- physical and mechanical abrasion resulting in physical breakdown, fragmentation and cracking that weaken the polymer structure and make it more susceptible to weathering and fragmentation, and subsequent abiotic and biotic degradation
- weathering and aging caused by oxidative degradation resulting from the formation of free radicals during exposure to solar radiation, temperature and certain chemical species.
- photo-oxidative degradation initiated by ultra-violet radiation. The sensitivity of polymers to photodegradation depends on their ability to absorb UV-A and UV-B radiation, and the type and quantity of chromophores and contaminants they contain (Shah et al, 2008).
- thermal degradation of plastics when they reach or exceed their melting temperature. This results in molecular deterioration of the structure and packing of the polymer. Since all but the most extreme environmental temperatures are considerably lower than the plasticity temperature of plastics the level of degradation by this means is typically very low.
- chemical degradation of plastics. This depends upon the molecular structure of the polymer, particularly the incorporation of oxygen via carbonyl or ester bonds, presence and quantity of contaminants, and environmental conditions. Through oxidation, oxygen molecules attack

and react with covalent bonds within the polymer structure of plastics to produce reactive oxygen containing functional groups. Oxygen can either react to produce reactive oxygen free radicals and/or react with free radicals produced in-situ within the polymer to produce reactive hyperoxides. Abiotic hydrolysis (reaction with water) is recognised as the most important reaction for initiating the environmental degradation of some synthetic polymers (Shah et al, 2008) but for most of the major types of synthetic polymers it typically requires high temperatures to proceed, and therefore the level of degradation by this means is typically very low under natural environmental conditions.

- biodegradation

5.1 Biodegradation of plastics

The biodegradation of plastics is dependent upon the characteristics of the polymer, the type of organisms, and environmental conditions, and the extent to which it has previously been subject to other degradation processes as described above. The establishment and growth of bacterial and fungal biofilms within pores, fissures and cracks on the surface of polymers produces mechanical fracturing which exposes additional surfaces that are quickly exploited and colonised by the increasing biomass, thereby increasing the rate of non-specific mechanical degradation. Biodegradation of plastics by enzymes produced by microorganisms is primarily dependent upon the molecular weight, crystallinity and hydrophobicity of the polymer. Enzymatic degradation of polymers proceeds by the action of extracellular and intracellular depolymerases. The biodegradation of polymers by microorganisms and the particular degradative pathways are often dictated by environmental conditions. In the presence of oxygen aerobic microorganisms dominate the degradation of plastic polymers to produce microbial biomass, CO₂ and H₂O. In the absence of oxygen (anaerobic conditions) anaerobic microorganisms dominate the degradation of plastic polymers to produce microbial biomass, CO₂, CH₄, and H₂O by methanogenic processes.

Numerous types of bacteria and fungi have been demonstrated to degrade natural and synthetic plastics. The biodegradation of plastics in the environment proceeds under a wide range of conditions according to their properties as the degrading microorganisms differ from each other and exhibit variable growth characteristics in response to environmental conditions. Important characteristics of polymers that effect their degradation include the degree of crystallisation, molecular weight, functional groups and other substituents in its structure, and the properties of chemical additives (Gu, 2003).

Because most polymers are too large to pass across cell membranes they must first be depolymerised to smaller subunits in order to be subsequently absorbed and biodegraded within the cells of microbes. In general, the biodegradation of polymers decreases with increasing molecular weight, whereas oligomers, dimers and monomers of polymers are much more easily degraded and mineralised by microorganisms. During biodegradation exoenzymes released by microorganisms attack and break down the polymer structure into smaller sized oligomers, dimers and monomers that can pass across cell membranes into the cells where intracellular enzymes break them down further to be utilised as carbon and energy sources (Shah et al, 2008).

Different types of microorganisms have been demonstrated to degrade polymers under different environmental conditions and a full discussion of these is beyond the scope of this report. Examples of the types of different microorganisms demonstrated to degrade different synthetic and

biodegradable plastics are listed in Table 6. References for the individual studies and identified microorganisms can be found in the review of Shah and co-authors (Shah et al, 2008).

Table 5: Types of microorganisms reported to degrade different types of synthetic and biodegradable plastic polymers

Synthetic Plastic	Microorganism
Polyethylene	<i>Brevibacillus borstelensis</i> <i>Rhodococcus rubber</i> <i>Penicillium simplicissimum</i> YK
Polyvinyl chloride	<i>Pseudomonas putida</i> AJ <i>Ochrobactrum</i> TD <i>Pseudomonas fluorescens</i> B-22 <i>Aspergillus niger</i> Van Tieghem F-1119
Polyurethane	<i>Comamonas acidovorans</i> TB-35 <i>Curvalaria senegalensis</i> <i>Fusarium solani</i> <i>Aureobasidium pullulans</i> <i>Cladosporium</i> sp. <i>Pseudomonas chlororaphis</i>
Biodegradable Plastic	Microorganism
Poly(3-hydroxybutyrate)	<i>Alcaligenes faecalis</i> <i>Schlegelella</i> <i>Thermodepolymerans</i> <i>Caenibacterium thermophilum</i>
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	<i>Clostridium botulinum</i> <i>Clostridium acetobutylicum</i>
Poly(lactic acid)	<i>Fusarium moniliforme</i> <i>Penicillium roquefort</i> <i>Amycolatopsis</i> sp. <i>Bacillus brevis</i> <i>Rhizopus delemer</i>

(Source: Shah et al, 2008)

In general, the rate and extent of biodegradation of polymers in the environment is determined by moisture content, availability of oxygen, temperature, salt concentration, and the type and density of microorganisms. Moisture content, availability of oxygen, and density of microorganisms have the greater effect on the rate of biodegradation, whereas the extent of biodegradation is determined by temperature and the presence or absence of eukaryotic (fungi) microorganisms. As a result the efficacy of biodegradation of plastics decreases in the order: compost (high temperature, thermophilic bacteria, fungi, high density of microorganisms) > soil (fungi, bacteria, moderate density of microorganisms) > fresh water (bacteria, relatively lower oxygen content and availability, low to moderate density of microorganisms) > marine water (relatively lower oxygen content and availability, and relatively dilute bacteria) (Deconinck and De Wilde, 2013).

5.1 Degradation of polyhydroxyalkanoate (PHA) type plastics

Several aerobic and anaerobic bacteria and fungi demonstrated to degrade PHA have been isolated from soil, activated and anaerobic sludge, seawater and lake water (Shah et al, 2008). Because PHA polymers are too large to be transported across bacterial cell walls these microorganisms excrete extracellular PHA depolymerases that degrade PHA polymers into water-soluble oligomer and monomer sub-units that microorganisms can absorb and use as a carbon source.

The isolation and characterisation of several PHB depolymerases that degrade PHA-type polymers (PHB, P(4HB) and PHBV) from various microorganisms demonstrates they are ubiquitous in the environment. PHB extracellular depolymerases are absorbed onto water insoluble PHA-type polymers via hydrophobic interactions. They degrade PHB polymers into mainly the dimer and a small quantity of the 3-hydroxybutyrate (3HB) monomer. The PHB degrading microorganisms also excrete extracellular dimer hydrolase which degrades oligomers and dimers of PHB polymer into the 3HB monomer (Matsumura, 2005) which is rapidly assimilated and mineralised by microorganisms.

Several strains of thermophilic bacteria that degrade PHA polymers have been isolated, confirming that PHB and PHBV polymers will biodegrade under composting conditions (Calabia et al, 2004; Tseng et al, 2007). Plastic films of PHB, PHBV, and blends of both, subjected to industrial composting conditions at the laboratory and pilot plant scale were readily populated by microbial biofilms, and rapidly disintegrated and lost weight within periods of six to seven weeks (El-hadi et al, 2002; Rutkowska et al, 2008; Weng et al, 2010). The observed weight loss was matched by biodegradation of the PHB and PHBV polymers films which reached 81% after 60 days under laboratory-scale composting conditions (58°C) and 100% biodegradation after twelve weeks under pilot-scale composting conditions (Weng et al, 2010).

The biodegradation of PHBV in soil is dependent upon the degradation ability of PHBV-degrading microorganisms that colonise its surface. The surfaces of PHBV films incubated in soil and sewage sludge amended soil have been observed to develop cavities and pits, surface roughening, and to ultimately disintegrate (Sang et al 2002; Molitoris et al 1996). An assessment of the biodegradability of different thermoplastic PHBV copolymers demonstrated the fastest rate of degradation was obtained for those polymers exhibiting the lowest degree of crystallinity and the roughest surface characteristics (Wang et al, 2004). These rough surface favour the attachment of microorganisms and the development of microbial biofilms, both of which precede and are important for subsequent microbial biodegradation.

PHBV has been demonstrated to completely degrade after 6, 75, and 350 days in anaerobic sewage, soil, and sea water, respectively (Lee, 1996). The degradation of the surface of PHB/PHBV blended films stored in river water was very similar to that observed during their burial in soil. Under aerobic conditions the extent of biodegradation of the PHB/PHBV varied from between 67 to 77% over a period of 60 days (El-Hadi et al, 2002). The degradation of blended films of PHB/PHBV films deployed in-situ in the Baltic sea ranged from 30 to 100% over a 6-week period and was lower than that obtained for the same films under composting conditions (Rutkowska et al, 2008).

High molecular weight PHB polymer is completely biodegraded and mineralised in river water within 28 days (Kusaka et al, 1999) and copolymers of 3HB and 4HB were completely decomposed in activated sludge within 2 weeks (Kunioka et al, 1989). PHBV polymer also degraded anaerobically in

aqueous media containing methanogenic sludge, with 99% biodegraded after 30 days as measured by the evolution of methane gas (Reischwitz et al, 1998).

5.1.1 Degradation products of PHA-type plastic polymers

Common metabolites identified from the degradation of PHB and PHBV copolyesters are the base monomers comprising their respective polymers, 3-hydroxy butyric acid and 3-hydroxy valeric acid.

Biodegradation of PHBV polymer by *Aspergillus fumigatus* (fungi) produced a number of low molecular weight transformation products including 3-hydroxy butyric acid, 2-hydroxy isobutyric acid, 3-hydroxy valeric acid along with the corresponding 3-hydroxybutyrate, 3-hydroxybutyrate-3-hydroxyvalerate and 3-hydroxyvalerate dimers. These chemicals continued to be released until the parent polymer was consumed, after which the corresponding series of organic acids 2-butenic acid, 2-pentanoic acid, and acetic acid were produced (Eldstate et al, 1997). Similar chemical by products have been observed during the biodegradation of PHB by Gram-positive bacteria and during enzymatic degradation by PHA depolymerase (Hakkarainen, 2002). With the exception of acetic acid, the same transformation products are produced from PHBV polymer under abiotic degrading conditions.

The anaerobic biodegradation of PHB and PHBV powders by an inoculum obtained from anaerobic sludge produced the same range of intermediate hydrolysis products including the dimeric esters of 3-hydroxybutyrate, 3-hydroxybutyrate-3-hydroxyvalerate and 3-hydroxyvalerate, and 3-hydroxybutyrate, and 3-hydroxyvalerate. These intermediary products were biodegraded by the consortia of anaerobic microorganisms to acetic, propionic, n-butyric and n-valeric acids which were able to be rapidly mineralised under anaerobic conditions to produce carbon dioxide and methane (Reischwitz et al, 1998).

There is no evidence that the dimer and monomer products produced from the degradation of and PHB and PHBV polymers are toxic or exert a negative impact on organisms exposed to them. The various oligomer, dimer, monomers and organic acids formed by the degradation of PHB and PHBV biodegradable PHA polymers are not inherently persistent or toxic and will be rapidly and readily biodegraded by numerous species of microorganisms in both terrestrial and aquatic environments.

5.2 Degradation of polylactic acid (PLA) plastics

During degradation, ester bonds of PLA must first be cleaved either hydrolytically or by extracellular enzymes to produce PLA monomers or oligomers that are able to be subsequently assimilated by microorganisms. Both parallel processes can be influenced by several factors. The enzymatically catalysed process depends on the presence of specific microorganisms, which are sparsely distributed in some environments (Husarova et al, 2014). The hydrolysis of PLA polymers has been widely reported and proceeds by random hydrolytic chain scission of the ester linkages at the C=O functional groups (Lv et al, 2017) and this process is dependent upon temperature and humidity, increasing with each or a combination of both. Degradation of PLA polymers by microorganisms in

the environment proceeds via this initial abiotic hydrolysis followed by microbial biodegradation (Madras, 2005).

Microorganisms that biodegrade PLA have a limited distribution and are relatively scarce in the environment in comparison to those that degrade PHA, PCL and PBS biodegradable plastics, but are widely distributed within the genus *Amycolatopsis* (Matsumura, 2005). During microbial biodegradation the PLA degrading microorganisms excrete extracellular enzymes that attack the intramolecular ester bonds of PLA to produce oligomers, dimers and monomer that transfer across microbial membranes into the microbial cells where they are converted by intracellular enzymes into aerobic or anaerobic mineralisation products.

Due to its use for the manufacture of compostable food packaging films, bags and containers the conditions under which PLA decomposes during composting conditions are well established (Tuominen et al, 2002; Karamanlioglu et al, 2017). PLA polymers are biodegraded during industrial large-scale composting processes when temperatures reach around 60°C. PLA is first degraded by hydrolysis to produce water soluble oligomers and lactic acid which are rapidly mineralised by a variety of microorganisms to water, carbon dioxide and biomass (Shah et al, 2008).

A number of studies have investigated the biodegradation of different types of PLA plastic products under various conditions. PLA plastic sheet (300µm thick) completely disintegrated within 34 days under industrial composting conditions, and the degree of biodegradation reached 86% after 4 months at 58°C under controlled laboratory composting conditions (Rudeekit et al, 2008).

In a recent study the biodegradability of PLA films incubated at 58°C over a period of 100 days under laboratory composting conditions was demonstrated to increase with decreasing molecular weight (MW) of the PLA polymer films. The % mineralisation of the PLA polymer films decreased from 95%, 85%, 55% and 60% respectively as the MW increased respectively from 34,000, 61,000, 109,000, to 160,000. The two higher MW PLA films exhibited a distinct initial lag phase of 20 days, whereas it was absent in the mineralisation curve for the lowest MW PLA film, and the mineralisation curve for the second lowest MW PLA film exhibited some acceleration after 20 days incubation. These results suggest that PLA with a MW of over approximately 60,000 is likely to experience a significant retardation of both the onset and extent of biodegradation (Husarova et al, 2014).

The biodegradation of PLA plastic bottles incubated in yard compost in laboratory bioreactors at 58°C and 55% relative humidity reached 64% after 63 days (Kijchavengkul et al, 2006), while the biodegradation of PLA plastic bottles cut into 1cm² pieces and composted at 58°C and 50-60% humidity under laboratory conditions reached 84% after 58 days. The mineralisation curve obtained for the biodegradation of the pieces of PLA bottle demonstrated a comparable initial lag phase of 15 to 17 days (Kale et al, 2007).

The degradation of PLA polymers during composting is improved by incorporating other biodegradable materials into the polymer structure. For example, the presence of corn in a PLA/corn bio-based polymer subjected to aerobic composting at a constant temperature of 58 ± 2 °C for 90 days increased the degree of bio disintegration from 64% to 80% compared to PLA polymer alone (Saras et al, 2009). In another study the biodegradability of PLA, PLA- wheat straw (70:30) and PLA- soy straw (70:30) bars (64 x 12.7 x 3.2mm L x W x H) was assessed within laboratory simulated composting conditions at 58°C. The degree of biodegradability for PLA and the PLA-straw composite

bars reached 90% but was achieved in 55, 70 and 100 days respectively for the PLA-wheat straw, PLA-soy straw and PLA only bars respectively (Pradhan et al, 2010). Similarly, incorporating poultry feather fibres into PLA polymer pots increased their biodegradability compared to PLA alone under aerobic composting (Ahn et al, 2014).

Similar observations have been made for the degradation of PLA polymers incorporating biodegradable materials in soil. The incorporation of sisal fibre into a PLA polymer resulted in > 50% higher weight loss following burial in soil for 14 weeks compared to PLA polymer alone (Wu, 2012). However, the observed increase in weight loss is almost certainly attributable to the preferential biodegradation of sisal fibre from the polymer, and not the PLA component.

The degradation of PLA polymers in soil is considerably less than that achieved under active composting conditions as the higher moisture content and temperature obtained during composting enhances the initial hydrolysis of PLA and the assimilation of PLA by thermophilic microorganisms (Itavaara et al, 2002). Soil burial experiments have shown there is a considerable lag time before the degradation of PLA begins and the degradation rate is relatively slow in soil (Ohkita & Lee, 2006).

For example, poly(L-lactide) (PLLA) films buried in soil in South Finland under environmental conditions did not produce lactic acid in the first year, indicating the highly crystalline structure of PLLA was not being degraded by hydrolysis to produce lactide oligomers or monomers. After 20 months burial in soil hydrolysis reactions produced lactic acid and lactoyl lactic acid, demonstrating initial hydrolysis of the PLLA polymer was the rate limiting step in its degradation. During this second phase of degradation soil microorganisms subsequently biodegraded the lactic acid and lactoyl lactic acid hydrolysis degradation products (Gallet et al, 2001).

Similarly, PCL, PBS and PBSA polymer films were considerably degraded in Japanese soil within 50 days at 25°C in the dark whereas a PLA film exhibited no signs of degradation after 120 days burial in soil (Kamiya et al, 2007).

The rate of weight loss observed for tensile bars of PLA-starch blends buried in soil for one year increased with increasing starch content (15 to 50%/year) but pure PLA bars exhibited no weight loss, indicating PLA polymer was not being degraded and the preferential biodegradation of starch in the PLA-starch blends was responsible for the weight loss of the polymer blends (Shogren et al, 2003). Similarly, the rate of degradation of PLA polymers in a Mediterranean soil under mild environmental conditions over an eleven-month period was very slow and resulted in mechanical degradation, but no biodegradation of PLA (Rudnik and Briassoulis, 2011).

Similarly, PLA buried in soil or compost at 25°C or 37°C for one year exhibited no change in tensile strength or molecular weight whereas all tensile strength was lost within 57 and 54 days respectively in soil and compost maintained at a higher temperature of 50°C (Karamanlioglu and Robson, 2013).

PLA is degraded very slowly and persists in soil as its temperature typically doesn't exceed 30°C. With the exception of biomedical applications most of the studies assessing the biodegradability of PLA polymers have been carried out under composting conditions at temperatures typically around 58°C.

Very few studies have investigated the biodegradation of PLA in aquatic ecosystems and those that have been completed suggest that like soil microorganisms, marine microorganisms have a limited ability to degrade PLA (Karamanlioglu et al, 2017)

Therefore, while it can be degraded and biodegraded under optimised composting conditions, PLA cannot be considered to be hydrolysable or biodegradable in soil, sediment and water under normal environmental conditions. This suggests PLA plastic products will accumulate in the environment and contribute to plastic pollution.

5.2.1 Degradation products of PLA polymers

PLA is synthesised from lactic acid by a condensation reaction or by ring-opening polymerisation of cyclic lactide monomer. The lactide monomer is a stereochemical, existing in three isomeric forms, which provides the means to adjust the physical and mechanical properties of PLA polymers, and their degradation rates. The chemical structures of lactide and several of the cyclic monomers it is commonly reacted with to produce PLA containing polymers are shown in Table 6. Of these PLA containing polymers only the PLA polymer itself is used in commodity products and the remainder are normally used for biomedical purposes.

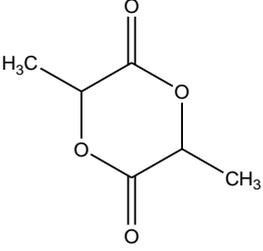
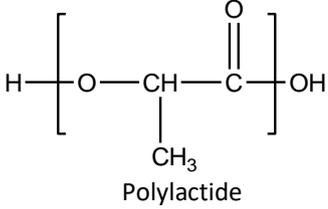
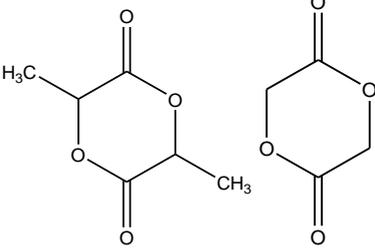
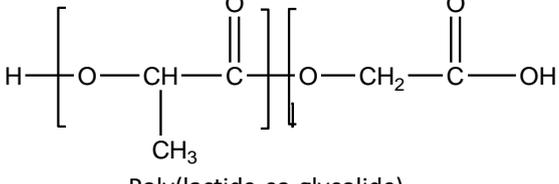
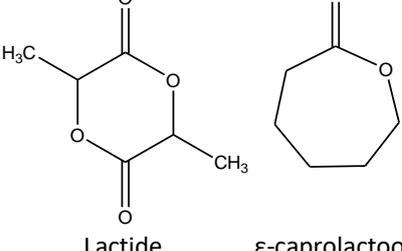
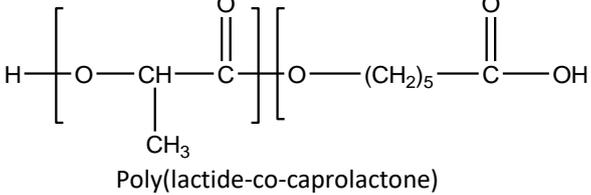
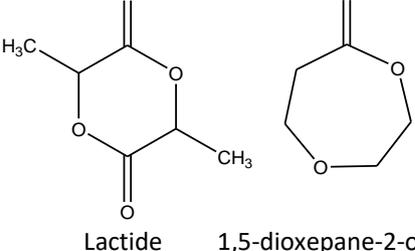
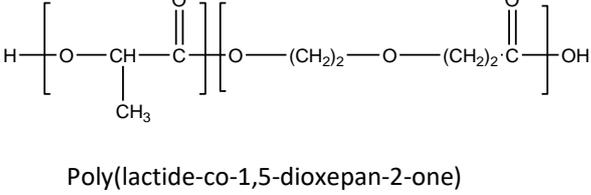
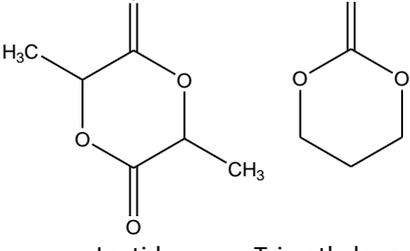
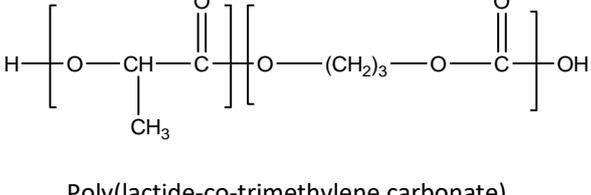
The degradation products formed by abiotic and biotic degradation of PLA and its co-polymers have been assessed in a number of studies. In abiotic aqueous environments the high molecular weight PLA polymer undergoes hydrolysis of the ester bonds to produce intermediate insoluble and soluble oligomers, and finally lactic acid (Hakkarainen et al, 1996).

The biodegradation of PLLA by a mixed culture of compost microorganisms produced lactide, acetic acid, propanoic acid and the ethyl ester of lactoyllactic acid. Acetic and propanoic acid were only produced as intermediary degradation products during the initial stages of biodegradation. Acetic acid, propanoic acid and the ethyl ester of lactoyllactic acid were not detected in a sterile abiotic control treatment and instead lactide, lactic acid and lactoyllactic acid were produced by abiotic hydrolysis. Under biotic conditions any lactic acid and lactoyllactic acid formed by abiotic hydrolysis of PLLA was rapidly assimilated by a mixed culture of compost microorganisms (Hakkarainen, 2002).

PLA polymer produced from a racemic mixture of L- and D-lactides (PDLLA) and exposed to a mixture of *Fusarium moniliforme* and *Pseudomonas putida* at 30°C produced DL- and L-lactic acids and a L,L-dimer that were rapidly assimilated by the microorganisms, whereas the assimilation of the sterically less favourable D,D-dimer proceeded more slowly (Torres et al, 1996).

PLA polymers produced by chain linkage reactions with 1,6-hexamethylene diisocyanate or 1,4-butane diisocyanate under controlled composting conditions degraded to over 90% of the positive control within 6 months. However, the biodegradation of PLA polymers produced with 1,6-hexamethylene diisocyanate as a chain linking chemical produced toxic responses in a microbial flash test and plant growth assays, attributed to residues of 1,6-hexamethylene diisocyanate in the final composted product. In comparison PLA polymers produced with 1,4-dibutane diisocyanate exhibited no toxicity (Tuominen et al, 2002).

Table 6: Types of monomers and resulting polymer repeat units in PLA polymers

Monomer	Polymer
 <p>Lactide</p>	 <p>Poly(lactide)</p>
 <p>Lactide glycolide</p>	 <p>Poly(lactide-co-glycolide)</p>
 <p>Lactide ε-caprolactone</p>	 <p>Poly(lactide-co-caprolactone)</p>
 <p>Lactide 1,5-dioxepan-2-one</p>	 <p>Poly(lactide-co-1,5-dioxepan-2-one)</p>
 <p>Lactide Trimethylene carbonate (TMC)</p>	 <p>Poly(lactide-co-trimethylene carbonate)</p>

Source: Hakkarainen, 2002.

Other chemical degradation products formed by the hydrolysis of various co-polymers of PLA include lactic and glycolic acids (from PLG copolymer), and 2-hydroxyethoxypropanoic acid and 3-(2-hydroxyethoxy)-propanoic acid (PLA-DXO copolymers) (Karlsson et al, 1994; Hakkarainen et al, 1996; Stridsberg and Albertsson, 2000).

The various oligomers, dimers, monomers and organic acids and esters produced by the degradation of PLA and PDLLA biodegradable polymers are not inherently persistent or toxic and will be rapidly and readily biodegraded by numerous species of microorganisms in both terrestrial and aquatic environments.

5.3 Degradation of oxo-degradable plastics

Oxo-degradation is a specific type of plastic degradation that harnesses photo-degradation by UV light and chemical oxidation to initiate the degradation of plastics with the intention to enhance their subsequent biodegradation. The degradation of oxo-degradable plastics proceeds by a chemical process called oxidative degradation. Oxidative degradation describes a complex combination of chemical reactions that break down the long chains of polymeric molecules into shorter lengths by the action of oxygen, UV light, and/or heat, and this process is catalysed and accelerated by the presence of oxo-additives (prodegradants) incorporated into the polymer structure during their production.

The larger proportion of commercial prodegradants are based on transition metals salts, the most common including iron, cobalt and manganese salts of fatty acid esters, amides and dithiocarbamates. The most commonly used fatty acid metal salts include acetates, stearates and oleates. These transition metals provide reactive sites that enhance the incorporation of oxygen into the carbon backbone of the polymer which ultimately results in them fragmenting into smaller pieces that are supposed to be more susceptible to continued abiotic (oxidative and hydrolytic degradation) and biotic degradation (biodegradation). The reaction with, and introduction of oxygen into the polymer, produces oxygen containing carboxylic, ester, aldehyde and ketone functional groups which changes them from being hydrophobic to hydrophilic, and therefore able to absorb water. These changes in the bulk surface properties of the polymer enable microorganisms to attach to them, establish biofilms on them, and begin to mechanically fracture the surface of the polymer, and modify the polymer chains.

Another term that is used in the literature to describe the degradation of oxo-degradable polymers is oxo-biodegradation. Oxo-biodegradation is used to describe a two-stage degradation process whereby the first phase of degradation is abiotic and involves the reaction of oxygen to oxidise the carbon backbone of the polymer. The second stage is the biodegradation of the modified oxidised polymer structure by microorganisms that attack the polymers at the oxygen containing positions of the carbon backbone fragments to produce biomass, carbon dioxide, and water. However, the claim that oxo-degradable plastics biodegrade is unconvincing for the following reasons. First, there is much uncertainty regarding the extent to which the fragments of residual oxo-plastics are subsequently colonised and biodegraded by microorganisms (Thomas et al, 2010). Secondly, oxo-degradable plastics are predominantly produced from PE and PP which as discussed below are

resistant to biodegradation. Thirdly, PE, PP and PS polymers used in oxo-degradable plastics do not meet any of the accepted standards (CEN, ISO, ASTM) for biodegradability or compostability.

Therefore, the use of the terms biodegradation or biodegradability by manufacturers of PE and PP oxo-degradable plastic products to describe the performance of their products post-use is at best misguided and at worst, misleading. This has been recognised by European Bioplastics, the organisation representing the European bioplastics industry who unequivocally state “There is currently no internationally established and acknowledged standard or certification process that proves the success of oxo-degradation. Without verifiable proof or certification for the claim, the term “oxo-degradable” is just an appealing marketing term” (European Bioplastics, 2015b).

It is well proven that following extended exposure to sunlight oxo-plastics become brittle and disintegrate into smaller fragments of residual plastic. The time required for oxo-plastics to fragment into small pieces of residual plastic depends on the physical structure (low or high density) and thickness of the plastic, and the type and concentration of prodegradants they contain.

Before discussing the specific mechanisms by which oxo-degradable plastics are designed to degrade it is first necessary to consider the processes by which the two base polyolefin polymers that predominantly make up oxo-degradable plastics, PE and PP, degrade.

5.3.1 Degradation of PE and PP

PE and PP are high molecular weight and hydrophobic polymers that are very stable and not biodegradable in their usual form. The biodegradability of PE and PP is improved by modifying their crystallinity, molecular weight and mechanical properties. This is achieved by reducing their hydrophobicity/increasing hydrophilicity and/or reducing their molecular weight and polymer chain length by oxidation so they can be assimilated by microorganisms (Shah et al, 2008).

Research on the degradation of polyolefins by microbes has mostly focused on PE because it is used much more frequently in large scale agricultural applications (particularly in agricultural films and mulches), for food packaging and wrapping, and single use plastic bags, than PP, and therefore is a major source of plastic litter and pollution.

The degradation of PE and PP occurs by the different chemical, thermal, photo and biodegradative mechanisms that have been previously discussed. Exposure to UV light and heat promotes the degradation of polyolefins like PE and PP, but they degrade extremely slowly under typical environmental conditions. For example, PE sheet subjected to UV-irradiation for 16 days prior to burial in soil emitted <0.5% CO₂ by weight after 10 years while the non-irradiated PE sheet emitted <0.2% CO₂ by weight (Albertsson and Karlsson, 1990). Similarly, a bottle produced of PE without prodegradants showed minimal degradation on its surface after being buried in soil for up to 37 years and PE film buried in soil for 32 years only partially degraded and at such slow rates it was estimated it would take around 300 years for a 60µm thick LDPE film to fully degrade in soil (Ohtake et al, 1998).

PE and PP have to undergo photo- or thermo-oxidation before they can biodegrade as only oxidised PE and PP degradation products of reduced molecular mass (500 to 5000 daltons maximum size) can

be degraded and assimilated by microorganisms (Ammala et al, 2011). It is widely accepted that abiotic oxidative degradation of PE and PP into lower molecular weight compounds is required before they can be degraded by microorganisms and/or enzymes.

Numerous studies have isolated and identified a wide range of different microorganisms that populate many different types of PE and are implicated in their biodegradation, some of which are summarised in Table 7.

Table 7: Summary of different microorganisms reported to populate and biodegrade PE.

Sample type	Microorganisms	Source
LDPE w/o prodegradants, thermal and/or UV pretreatment	<i>Gliocladium virens</i> ATCC 9645 <i>Aspergillus niger</i> ATCC 9642 <i>Penicillium pinophilum</i> ATCC 11797 <i>Phanerochaete chrysosporium</i> H289	Culture collection
LLDPE w/6% starch prooxidant	<i>Phanerochaete chrysosporium</i> ME 446 <i>Streptomyces viridosporous</i> ATCC 39115	Culture collection
UV and thermal treated	<i>Streptomyces badius</i> ATCC 39117 <i>Streptomyces setonii</i> ATCC 39116	
LDPE, LLDPE w/cobalt acetylacetonate: thermal pretreatment	<i>Aspergillus niger</i> ATCC 6275 <i>Gliocladium virens</i> ATCC 9645 <i>Paecilomyces variotii</i> 10121 <i>Penicillium funiculosum</i> ATCC 39115 <i>Streptomyces</i> strain	Culture collection
LDPE w/prooxidant	<i>Pseudomonas aeruginosa</i>	Culture collection
HDPE	<i>Phanerochaete chrysosporium</i>	Culture collection
LDPE Fe prooxidant	<i>Cladosporium cladosporoides</i> ATCC 20251	Culture collection
PE w/6%wt starch, thermal pre-treatment	<i>Mucor rouxii</i> 1835 <i>Aspergillus flavus</i>	Culture collection
LDPE w/starch/Fe sterate thermal pre-treatment and LDPE w/starch, Mn stearate, w/styrenebutadiene co polymer thermal pre-treatment	<i>Arthrobacter paraffineus</i>	Paraffin wax degrading
LDPE w/photosensitiser thermal and UV pre-treatment	<i>Rhodococcus ruber</i> <i>Brevibacillus borstelensis</i>	Soil
HDPE UV and thermal pre-treatment	<i>Penicillium simplicissimum</i> YK	Soil
LDPE w/prooxidant UV and thermal pre-treatment	<i>Rhodococcus</i> sp.	Soil
LDPE w/60% Bionella	<i>Aspergillus niger</i>	Soil
LDPE w/cobalt stearate UV pretreatment	<i>Bacillus pumilus</i>	Soil
LDPE and HDPE Unpre-treated and thermal treatment, unpre-treated and starch-blended	<i>Bacillus sphericus</i> GC subgroup IV <i>Bacillus cereus</i> subgroup A	Marine
LDPE thermal pre-treatment	<i>Rhodococcus ruber</i>	Laboratory isolate
PE wax	<i>Bacterial consortium KH-12</i>	

Adapted from Ammala et al, 2011.

The stability of PE to biodegradation is further evidenced by its relative resistance to biodegradation by thermophilic microorganisms. PE incubated with a thermophilic bacterium (*Brevibacillus borstelensis* strain 707) for 30 days at 50°C reduced its gravimetric and molecular weights by 11 and 30% respectively (Hadad et al, 2005). However, laboratory-based experiments do not reflect real

environmental conditions, a complex microbial community, and the variable abiotic and biotic factors that combine to influence the biodegradability of PE and PP.

There are very few reports of the microbial degradation of PP and those that have been completed have assessed the degradation of PP co-polymer blends or PP containing prodegradant additives. The bacterium *Stenotrophomonas panacihumi* PA3-2 isolated from soil from a municipal waste field was demonstrated to degrade low molecular weight polypropylene polymers (10,300 and 19,700) during composting at 37°C for 90 days. The biodegradation of PP, assessed by the evolution of carbon dioxide, was dependent upon the average molecular weight of the polymers with 20.3%, 16.6% and 12.7% being biodegraded for polymers with Mw of 10,300, 19,700 and 228,000 respectively (Jeon & Kim, 2016). Therefore, while it is far from common, it is possible for PP to be biodegraded by soil bacterial microorganisms.

It is evident from numerous studies that the rate of degradation of typical unmodified PE and PP plastics is extremely slow under normal environmental conditions and their degradation products will persist for many decades and potentially hundreds of years in the environment.

Enzymes

High molecular weight polymers are not susceptible to intracellular enzymatic biodegradation as they are too large to transfer across cell membranes. Instead microorganisms secrete extracellular enzymes that attack polymer chains to produce reactive free radicals that break apart the polymer chains and produce smaller sized oligomers, dimers and monomers.

While there are numerous reports of the establishment of microbial biofilms on the surface of different forms of PE that subsequently utilise the lower molecular weight degradation products of polymers, there is limited information on the specific enzymes involved in the degradation process. Enzymes reported to degrade PE include extracellular polyethylene degrading enzymes produced by a lignocellulose degrading *Streptomyces* species and manganese peroxides produced by the lignin degrading fungi ZU-154 and *Phanerochaete chrysosporium* (Ammala et al, 2011). Recently two fungal isolates, *Penicillium oxalicum* NS4 (KU559906) and *Penicillium chrysogenum* NS10 (KU559907) extracted and isolated from the soil of a plastic dump site were demonstrated to degrade sheets of both LDPE and HDPE. The percentage of the total weight loss of HDPE and LDPE sheets after 90 days of incubation with the fungal isolate NS10 was 58.6% and 34.4% respectively, and 55.3% in HDPE and 36.6% in LDPE sheets by the fungal isolate NS4 (Ojha et al, 2017). While the authors postulated the mechanisms of degradation were the product of enzymatic degradation and solubilisation of PE they did not undertake analysis of potential enzymes to confirm their conclusion.

PP exposed to two different fungal strains for 1 year displayed both gravimetric and thermogravimetric weight loss, the latter of which correlated with the mass of biomass and the amount of laccase produced by the fungal strain (Jeyakumar et al, 2013).

There is a paucity of information on the exact role that enzymes play in the degradation of PE and PP and further research on this subject is required to better understand the role of microbes and the underlying mechanisms by which they can degrade PE and other polyolefin polymers like PP.

Mechanism of biodegradation

Due to the current lack of knowledge on the role of microorganisms and the enzymes they produce there is ongoing debate about the biodegradative mechanisms of PE and PP.

Present day understanding of the biodegradation of PE is based on an earlier study where it was proposed that because PE has a similar linear structure to paraffin molecules it is likely they will have similar biodegradation mechanisms and can be biodegraded by similar microorganisms (Ammala et al, 2011). Under this proposed biodegradation mechanism microorganisms and/or enzymes they produce attack abiotically oxidised and degraded PE to eventually produce fatty acids that transfer into cells where they are mineralised into carbon dioxide, water and biomass. However, there are significant differences between the properties and stability of higher molecular weight polyolefin polymers like PE and PP, and low molecular weight paraffinic waxes, as demonstrated by their relative thermal stability.

It remains unclear if LDPE is assimilated in a similar manner to paraffins by microorganisms or if it is further degraded by abiotic or biotic processes into smaller molecules that are subsequently absorbed by microorganisms and transported inside their cells. It has also been proposed that lignolytic enzymes produced by lignin-degrading microorganisms could degrade PE and other polyolefins. This is debatable as the structure of lignin is composed of three core methoxylated aromatic monomers that are crosslinked by numerous ester bonds, whereas PE, PP and other polyolefins consist of long uninterrupted chains of chemically stable hydrocarbon-based monomers.

Our understanding of the biodegradation of PP is further confused by previous assessments being carried out on commercial PP products containing various stabilising and or prodegradant additives, so the result obtained do not reflect the biodegradability of PP alone.

Our limited understanding of the specific mechanisms by which PE and PP are biodegraded by microorganisms represents a significant knowledge gap that hinders our ability to improve our understanding of their fate and impact in the environment, and to develop PE and PP products that could biodegrade and provide improved environmental outcomes.

5.3.2 Biodegradability of oxo-degradable plastics

The polymers predominantly used in oxo-degradable plastic product are low density polyethylene (LDPE), linear LDPE (LLDPE), high density PE (HDPE), polypropylene (PP) and to a lesser extent polystyrene (PS) (Wiles, 2005b). Due to its predominant use in oxo-degradable plastic products the following discussion focuses on oxo-degradable PE based plastics.

The biodegradability of oxo-degradable plastics can only occur after they have fragmented into smaller pieces and subsequently lower molecular weight polymer sub-units, after which it proceeds very slowly as determined by the properties of the base polymer. The evidence demonstrating that oxo-degradable plastics physically degrade and fragment upon exposure to sunlight and heat for extended periods of time is incontrovertible, the oxidative mechanisms are well researched and understood, and it is known the oxidative degraded polymer becomes brittle with time and

disintegrates into small fragments (Abrusci et al, 2013; Chiellini et al, 2006; Corti et al, 2010 & 2012; Koutny et al, 2006; Yashchuk et al, 2012).

There are numerous papers reporting that oxo-degradable plastics are populated and readily assimilated and biodegraded by microorganisms following this initial phase of oxidation (Chiellini et al, 2003 & 2006; Eyheraguibel et al, 2017; Fontanella et al, 2010; Koutny et al 2009; Roy et al, 2008; Portillo et al, 2016). In these studies, the oxo-degradable films have been pre-exposed to UV light or heat, simulating artificial weathering, to advance the aging and oxidative degradation process prior to assessing their biodegradation by microorganisms.

The extent of biodegradation of oxo-degradable PE plastics reported in the literature is variable, ranging from 5 to 60%. This range in biodegradability reflects differences in experimental design, pre-weathering and oxidative treatment of test materials, characteristics of the test material, methods used to assess degradation, and the use of poorly controlled abiotic and biotic conditions. In part, this has led to the development of standards specifying controlled conditions under which to assess the biodegradability of plastics.

Additionally, differences in the composition and formulation of polymers have a direct effect upon their biodegradation. For example, linear polyolefins subjected to natural weathering undergo different degrees of oxidative degradation depending upon their composition with PP, oxo-HDPE, and oxo-LLDPE degrading more rapidly than HDPE and LLDPE (Ojeda et al, 2011). Similarly, LDPE and LLDPE containing prodegradants oxidise more efficiently than HDPE and subsequently biodegrade at a faster rate (Fontanella et al, 2010).

A large proportion of studies investigating the degradability of oxo-degradable plastics base their claims of biodegradability on changes to bulk physical characteristics (surface area, molecular weight distribution, elemental and functional group composition-particularly increased carbonyl content etc.) of the tested polymers. For example, the decrease in the molecular weight (MW) of polymers incubated in soil and/or compost mixtures is attributed in numerous scientific papers to the action of bacteria with the conclusion that microorganisms have cleaved the high MW polymer chains into shorter chain lengths. The authors often extend this conclusion further, stating the observed reduction in MW of the oxo-degradable polymer means it is now able to be fully biodegraded by microorganisms.

Studies assessing the biodegradability of PE films that were subjected to abiotic oxidative pre-treatments and/or containing different pro-degradant additives and exposed to PE degrading microorganism found the MW of the PE films reduced considerably following abiotic oxidative treatment (Yamada-Onodera et al, 2001; Chiellini et al, 2003; Kawai et al, 2004; Reddy et al, 2009). Analysis and comparison of the MW distribution of abiotically oxidised and degraded PE polymer before, during and after biodegradation assessments in culture media, soil, and compost, clearly show the exposure of pre-treated PE to microorganisms results in a depletion of low MW polymer components produced by abiotic degradation, and retention and preservation of high MW components of the polymer (Yamada-Onodera et al, 2001; Chiellini et al, 2003; Jakubowicz et al, 2003; Kawai et al, 2004; Reddy et al, 2009). The rate of molecular weight reduction of thermally oxidised PE increases, and the final average MW decreases with increasing temperature during abiotic oxidative pre-treatment (Jakubowicz et al, 2003). In another study it was observed there were no significant differences in the molecular weight distribution between abiotic control

treatments and biodegradation treatments of PE film subjected to abiotic oxidative pre-treatment (Fontanella et al, 2010).

These various studies demonstrate microbial biodegradation of the previously oxidised and abiotically degraded PE films is superficial and involves the biodegradation of lower MW polymeric sub units released from the previously abiotic oxidised polymer, and not by microbial degradation of the residual base polymeric structure. These studies clearly demonstrate microorganisms are unable to assimilate and biodegrade PE polymer residues with MWs above 3000 Da, and residues of PE polymer above this MW are resistant to biodegradation and will persist and accumulate in soil and compost.

Most studies of the biodegradability of oxo-degradable plastics have been conducted using specific isolated and enumerated microorganisms under controlled lab conditions (particularly temperature), that are optimised to maintain a high and sustained level of microbial activity. Some of these studies have isolated potentially efficient degrader microorganisms from environments contaminated with plastics, for example plastic dumps and landfills. Such assessments have little relevance to processes occurring in the natural environment where the microorganisms within the microbiome compete for available resources. Also, the procedures used to enumerate, and isolate specific degrading microorganisms can induce a level of degradative capacity for a particular polymer that would otherwise not be expressed within natural environments that contain a myriad of different and more accessible organic substrates for microorganisms to assimilate.

The most rigorous and reliable means of assessing the biodegradation of oxo-degradable and other polymers are obtained by directly measuring the CO₂ evolved during the biodegradation and mineralisation process. Studies assessing the biodegradation of oxo-degradable plastics in soil and compost using the consortia of native microorganisms that populate them provide a more realistic assessment and estimation of their biodegradability by microorganisms populating real-world environments. The studies that have been completed to date clearly show that PE degrades slowly in soil and compost and is far from complete.

For example, PE film (30µm thickness) containing Mn-stearate prodegradants pre-treated by thermal oxidation at 70°C for 4 weeks and subsequently incubated in soil at 60°C for 200 days, reached maximums of 60.3% and 65.1% biodegradation with the higher value obtained for PE film containing twice the quantity of pro-degradant (Jakubowicz et al, 2003).

LDPE containing the “totally degradable plastic additives” (TDPA™) from EPI Inc. that was subjected to abiotic thermo oxidation pre-treatment (44 days at 55°C) followed by incubation in a forest soil at room temperature biodegraded more slowly and to a much lesser extent compared to a filter paper control. After 30 days of incubation only 4% of the LDPE polymer had biodegraded and mineralised to CO₂, and further biodegradation ceased. Mineralisation of LDPE was restarted after 5 months of incubation upon the addition of fresh forest soil and water which introduced fresh microbial inoculum and a food source to stimulate and maintain their activity. LDPE in soil that only received additional water reached a maximum of 49% mineralisation while LDPE that received the addition of both water and fresh forest soil reached a maximum of 63% mineralisation after 85 weeks (595 days) incubation (Chiellini et al, 2003).

An international study funded by the European Union demonstrated the biodegradation of oxo-degradable PE film (36µm thickness) in soil reached a maximum of 15% after 200 days incubation at 28°C and did not increase thereafter up to 350 days incubation (Feuilloley et al, 2005).

The biodegradation of previously oxidised HDPE, LDPE and LLDPE films containing various prodegradants in soil incubated at 25°C reached maximums of <5%, 9% and 12% mineralisation respectively for the HDPE, LDPE and LLDPE films after 317 days incubation (Fontanella et al, 2010). In compost incubated at 58°C for 317 days the corresponding maximum levels of mineralisation were <6%, 16% and 24% respectively for the HDPE, LDPE and LLDPE films.

LDPE and HDPE plastic bags containing prodegradant oxidising additives exposed to natural weathering by sunlight and heat for one year followed by composting at 58°C biodegraded to a maximum of 12.4% after 3 months incubation. However, at a temperature of 25°C which is more representative of temperate climates, the corresponding maximum level of mineralisation was only 5.4% (Ojeda et al, 2009).

In comparison, oxo-degradable PE films and plastic bags, pre-exposed to UV light and heat, followed by composting in a bioreactor at 55°C reached a maximum of 24% mineralisation after 90 days incubation. PE without prodegradants subject to the same oxidative and composting treatments biodegraded at a slower rate than PE containing prodegradants for the first 20 days after which the biodegradation profiles for both were matched and they attained the same level of 24% mineralisation (Yashchuk et al, 2012). In a subsequent study Portillo (Portillo et al, 2016) assessed the biodegradation of PE films with and without prodegradants, and with and without abiotic oxidative pretreatment (UV light and heat) in compost within a bioreactor maintained at a temperature of 55°C for 120 days. Plateaus in the mineralisation profiles and maximum levels of mineralisation were 60 days and 6%, 100 days and 4% and 110 days and 21%, respectively for PE with prodegradants and no abiotic pretreatment, PE without prodegradants but abiotically degraded, and PE with prodegradants and abiotically degraded.

Most of the studies reporting biodegradation of oxo-degradable PE plastics in soil or compost have employed PE that has been “pre-aged” or pretreated by UV light and heat, most often employing conditions (UV intensity and temperatures) that have little or no relationship with those prevailing in environments they will be used in, or accumulate within as plastic litter. Many studies pre-treat and oxidise oxo-degradable plastics at temperatures ranging from 70°C to 100°C for several weeks- such temperatures do not occur within the warmest of climates on the planet.

For example, in the South of France in July 2001 the temperature of soil 10cm below the surface was 1.1°C higher than the ambient air temperature. At 50cm depth it attained a maximum temperature of 5.2°C below the maximum air temperature, equivalent to 35°C during the hottest two hours of the day (Feuilloley et al, 2005). Similar unrealistic levels of UV light intensity and duration are applied to pre-age oxo-degradable plastics before subjecting them to biodegradation tests. Within agricultural systems as much as 30 to 50% of the volume of oxo-degradable plastic films is buried within the soil and not exposed to UV light. The area of exposed oxo-degradable plastic films is only exposed to UV light for the relatively short time it takes for a crop to establish after which it becomes increasingly covered by vegetative growth and protected from UV light and heat.

The use of such extreme pre-treatment conditions in these biodegradation studies of oxo-degradable plastics is justified necessary to simulate and accelerate advanced aging and weathering processes that occurs in the natural environment. Unfortunately, the real-time equivalent of such accelerated aging is rarely provided, so it is impossible to ascertain how realistic and representative these pre-treatments are of real-world exposures to sunlight and heat. If accelerated thermal and UV pre-treatment conditions of three weeks duration represents the equivalent of 3 years of exposure and weathering under natural environmental conditions this implies an oxo-degradable plastic could potentially remain fully intact for at least 3 years in the environment.

This is confirmed by a study that demonstrated the time required for oxo-degradable PE films to degrade to a MW of 10,000 by abiotic oxidative processes at a temperature of 60°C was 18 days for a PE film containing Mn-stearate prodegradant, and 11 days for PE film containing twice the content of Mn-stearate prodegradant. The time required for these PE prodegradant containing films to reduce to a MW of 10,000 by abiotic oxidative processes at the lower temperature of 25°C was 4.5 years and 2.5 years (Jakubowicz et al, 2003). At this point the sub-unit residues of the PE films (>10,000 MW) will not be able to be biodegraded by microorganisms and will persist and accumulate in the environment.

The best indications of the timeframe and extent to which oxo-degradable plastics will degrade or persist under real-world environmental conditions is provided by the widespread use of oxo-degradable PE films as mulching covers in agriculture. These oxo-degradable plastic mulch films are constantly exposed to environmental levels of heat, light, water, wind, the abrading action of soil particles and stones, and mechanical wear from cultivation practices.

Oxo-degradable LLDPE residues buried for 7, 8 or 8.5 years following exposure to ambient light and heat during the cultivation of a watermelon crop exhibited a significant reduction in mechanical properties rather than chemical breakdown, and successively broke down to smaller fragments to produce microplastics (MPs) in soil (Briassoulis et al, 2015a). In another field study LLDPE mulching films containing prodegradants and exhibiting a loss in mechanical properties during cultivation were artificially degraded to simulate severe degradation/fragmentation resulting from many years burial in soil, followed by burial in a field soil for 7 years. The artificially abiotic degraded LLDPE oxo-degradable plastic film pieces were successively transformed into visible and invisible micro-fragments in the soil. In contrast, LLDPE oxo-degradable plastic film that was not artificially abiotically degraded prior to burial in soil remained intact for up to 8.5 years (Briassoulis et al, 2015b).

These studies confirm that oxo-degradable polyolefin-based plastics will fragment in soil due to combined abiotic oxidation and mechanical aging but remain resistant to biodegradation by environmental microorganisms. A similar conclusion was reached in a comprehensive report prepared for the UK Department for Environment Food and Rural Affairs on the environmental impacts of oxo-degradable plastics which stated that “oxo-degradables cannot be described as compostable and to describe them as biodegradable is likely to be confusing to consumers” (Thomas et al, 2010).

If oxo-degradable plastics do begin to biodegrade in the environment it will be at a very slow rate and to a very limited extent. During the biodegradation process the low molecular weight compounds and components that are produced and released from the oxo-degradable polymer by

abiotic oxidative degradation will be utilised by microorganisms. Increased weathering of oxo-degradable plastics by thermal oxidation and/or exposure to UV light will increase the quantity of low molecular weight material that is produced, which will subsequently increase the rate and extent of apparent biodegradation.

The fragmented residues of oxo-degradable plastic will persist in the environment for possibly decades and will ultimately accumulate in the environment as MP residues. Therefore oxo-degradable plastics cannot be described as biodegradable or environmentally degradable (Steinmetz et al, 2016). This level of persistence of oxo-degradable plastic products would undoubtedly be unacceptable to consumers and the public who will expect significantly reduced timeframes for products advertised and marketed as being degradable.

There is an absence of studies in which oxo-degradable plastics have been aged and weathered under real field conditions prior to being subjected to biodegradation assessments. It is therefore difficult to draw conclusions from the limited studies that have been completed about the extent and timeframes in which biodegradation of oxo-degradable plastics will occur in the natural environment and the rate and quantity of at which they produce MP residues.

Investigations of the biodegradation of PE and other polyolefin oxo-degradable plastics under real world conditions are complicated by methodological problems arising from the need to carefully monitor slow processes occurring on the surface of polymeric materials. The durability of PE and other polyolefin polymers means long-term experiments need to be implemented to reliably assess their biodegradability. Such experiments are incompatible with short to medium term funding strategies, the competing level of R&D investment available to the polymer industries, and the rate at which they introduce and release new products into the market place.

As a result, and in the absence of firm regulation on their use and disposal, the production and use of oxo-degradable PE products will grow considerably before we have sufficient knowledge of their environmental fate and impact, and the true risk they present within ecosystems they degrade, persist and accumulate within.

5.3.3 Degradation products of oxo-degradable polyolefin plastics.

Very few studies have investigated the chemicals produced from the degradation or biodegradation of oxo-degradable polyolefin plastics, or their potential fate and impact in receiving environments. Consequently, a major review of the environmental impact of oxo-degradable plastics prepared for the Department for Environment, Food and Rural Affairs in the UK found no evidence that oxo-degradable plastic fragments have a harmful environmental effect, but neither was there evidence they do not (Thomas et al, 2010).

The chemicals that have been identified from the degradation of oxo-degradable polyolefin plastics include straight chain and branched saturated and unsaturated alkanes (C15 to C26), a range of corresponding shorter chain fatty acids (i.e. octanoic acid), alkyl ketones (i.e. 3-dodecanone), and alkyl alcohols (i.e. eicosanol) (Albertsson et al, 1995; Roy et al, 2008), and the plasticisers benzyl butyl phthalate, butyl-8-methylnonyl phthalate, diisooctyl phthalate and dioctyl adipate (Albertsson et al, 1995). Apart from phthalate esters these chemicals are natural compounds common to many

soils, are not toxic, will be rapidly biodegraded by soil microorganisms, and present no environmental risk. In comparison residues of phthalate esters have been demonstrated to persist in soil under certain conditions, they can bioaccumulate in organisms exposed to them, and have endocrine disrupting properties.

Oxo-degradable polyolefin plastics contain transition metal salts of Fe, Co, Ni and Mn as prodegradant additives that promote their abiotic degradation upon exposure to sunlight and/or heat. While concern regarding the release and fate of these metals has been expressed it is important to recognise these are transition metals and not toxic heavy metals, and they are widely present in soil, drinking water and all manner of foods. These transition metals are typically present in oxo-degradable plastics at such low concentrations that the soil concentration of nickel would increase by 1ppm following 500 years continual use of an oxo-degradable PE mulching film containing nickel dialkyldithiocarbamate as a prodegradant additive.

It is widely confirmed that the fragmentation of oxo-degradable PE and other oxo-degradable polyolefin plastics produces residues of MPs. There is considerable uncertainty and increasing concern regarding the fate and potential impact of MP residues in the environment. While the producers of oxo-degradable plastics claim the plastic fragments they produce are benign and beneficial as they contribute additional organic carbon and humus in soil, there is a paucity of knowledge about their long-term effects in soil, and particularly within productive agroecosystems (Steinmetz et al, 2016).

Potential impacts of oxo-degradable plastic fragments and MPs in the environment include their ingestion by earthworms, invertebrate insects, birds and other animals. Fragments of oxo-degradable polyolefin plastics and MPs they produce may concentrate and increase the persistence of pesticide residues in soil within agrosystems. These fragments and MPs may migrate from soil and be transported via macropore and/or preferential flow pathways into groundwater, or via overland flow from terrestrial into freshwater and marine ecosystems where they will accumulate and may exert an impact upon aquatic biota.

It is widely repeated in the research literature that when polyolefin polymers degrade to produce polymeric sub-units < 5000 molecular weight they are readily and rapidly assimilated and metabolised by microorganisms. But there is an absence of studies assessing the formation, fate and effects of persistence polymeric residues >5,000 MW within terrestrial and aquatic ecosystems. The absence of such studies represents another significant gap in our knowledge of the potential environmental impact of oxo-degradable plastics.

To date there are no studies attempting to quantify the production, let alone the impact, of MPs resulting from the degradation and fragmentation of oxo-degradable plastics in compost or soil. Based on the evidence presented in this report it is highly likely that oxo-degradable plastics containing polyolefin polymers like PE and PP are a significant source of MPs within the environments they are either used in or accumulate within. If investigated in detail, it is entirely plausible that MPs from this source will be found to be as equally pervasive in terrestrial environments as they have been found to be in freshwater and marine environments (Nizzetto et al., 2016).

5.5 Additives in biodegradable and oxo-degradable plastics

Plastics do not only consist of polymers. Plastics are produced from a base polymer that also contain metals that catalyse the polymeric reaction and various additives to improve the processing properties of the plastic polymer (melting, moulding, extruding, and setting agents) and to improve the performance and durability of the final plastic material. In many cases the properties of the plastic alone are sufficient to make them fit for purpose. This is particularly true for many single use packaging plastic materials where only small amounts of specific additives are added, for example, to reduce oxidation and improve slip properties (reduce surface friction) during and after their production. With the exception of plastics produced for *in-vivo* applications (largely medical) it is doubtful that any plastic materials, including biodegradable and oxo-degradable plastics, are produced without additives (Wiles, 2005a).

For other applications it may be necessary to improve the basic properties of plastic polymers by incorporating a greater number and higher quantities of certain additives. Some can be added to improve the resistance of plastic materials to fire or provide greater protection from damaging UV light or exposure to heat. Consequently, most commercially produced plastics will contain several types of additive with each performing a specific task. Most additives in plastic can be classified into the following classes:

- functional additives (anti-oxidants, thermal and UV stabilisers, slip agents, curing agents, foaming agents, lubricants, anti-static agents, flame retardants, plasticisers, biocides etc.)
- colorants (inorganic pigments, azo-based dyes etc.)
- fillers (mica, talc, minerals, clay etc.)
- reinforcements (wood or plant, glass, carbon fibres)
- prodegradants

Biodegradable and oxo-degradable plastics do not begin to degrade in storage, in use, or immediately within the environment, because like traditional fossil fuel plastics they contain additives that make them fit for their intended purpose and stable over their expected lifetime. Oxo-plastics will not begin to break down until the stabilising additives they contain become depleted and they lose their protective capabilities. Other additives, particularly phthalate acid ester plasticisers, impact specific properties of plastics, for example flexibility in plastic films and tubing.

Almost all the additives incorporated into plastics are industrial high production chemicals. Examples of some of the high production chemicals in three classes of additives that are commonly incorporated into PE and PP plastics are listed in Table 8.

Most high-use biodegradable plastic is used for food packaging and requires the disclosure of all intentionally added ingredients, together with assessments of their potential to migrate into food. While it is unlikely that high-volume high-use biodegradable and oxo-degradable plastic packaging products would contain organic dyes, flame retardants, or plasticiser additives, it is extremely

difficult to obtain information on what additives they do contain. However, these types of plastics will contain various processing, antioxidant and stabiliser additives.

These additives are common ingredients in many different types of plastics and a wide range of different plastic products from numerous plastic manufacturers. Other high-volume high-use consumer products, for example personal care products, list the major and minor ingredients they contain on the product packaging. In comparison, plastic products do not provide such information, nor do they provide information on the source or composition of their main formulary ingredients, for example Masterbatches of pigments, colourants or additives, they contain.

Information on the types of additives and the composition of ingredients and materials used in the manufacture of polymers that are incorporated into different plastic products is very difficult, if not impossible to obtain. The absence of this information and the challenges this presents to identifying non-intentionally added substances in food packing materials has been previously recognised (Nerin et al, 2013). The manufacturers of plastic and the plastic industry have this information but justify not making it available to the public on the basis of commercial sensitivity. This issue was recently highlighted by the OECD which stated “One related, more general concern with additives (in plastics) is the lack of transparency and information about what additives are being used in different materials” (OECD, 2018).

Table 8: Examples of chemical additives that have been used in PE or PP based plastic products.

Antioxidants	
2,2'-Ethylidene-bis(4,6-di-tert-butylphenol)	35958-30-6 ^A
Pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)	6683-19-8
Didodecyl 3,3-thiodipropionate (DLTDP)	123-28-4
N,N-Dibenzylhydroxylamine	621-07-8
Reaction mass of Bis(2,4-bis(2-methylbutan-2-yl)phenyl) 4-(2-methylbutan-2-yl)phenyl phosphite and 2,4-Bis(2-methylbutan-2-yl)phenyl bis(4-(2-methylbutan-2-yl)phenyl) phosphite and Tris(4-(2-methylbutan-2-yl)phenyl) phosphite.	939402-02-5
4,4'-(2,2-propanediyl)diphenol	96152-48-6
Tris(2,4-di-tert-butylphenyl) phosphite	31570-04-4
Bis(2,6-di-ter-butyl-4-methylphenyl)pentaerythritol-diphosphite	80693-00-1
Photostabilisers	
Benzophenone	119-61-9
Benzotriazole	95-14-7
2,2,6,6-Tetramethyl-4-piperidiny l stearate	167078-06-0
Poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol-alt-1,4-butanedioic acid)	65447-77-0
Flame retardants	
2,4,6-Tris-(2,4,6-tribromophenoxy)-1,3,5-triazine	25713-60-4
2,2',6,6'-Tetrabromobisphenol A diallyl ether	25327-89-3
Dechlorane Plus	13560-89-9
Ammonium polyphosphate	68333-79-9
Tris(4-isopropylphenyl)phosphate	68937-41-7

^ACAS number

(Adapted from Ambrogi et al, 2017).

While manufacturers of plastic products readily provide the names for controversial ingredients their products do not contain, for example “Bisphenol-A free”, they are less forthcoming about the

chemical additives their products do contain. This practise is puzzling as most additive chemicals are present in plastic products at significant concentrations ranging from 0.5 to 5 % by weight (antioxidants, UV stabilisers, heat stabilisers, lubricants, colourants) and as high as 3 to 25% for flame retardants and 10 to 70% for plasticisers (Hahladakis et al, 2018).

With the exception of plastics destined for food contact or packaging purposes many of the chemical additives incorporated into plastic are known toxicants (for example anthraquinone and azo dyes, brominated flame retardants) or endocrine disrupting chemicals (plasticisers, Bisphenol-A, Benzophenone type UV stabilisers, nonylphenols etc.). These chemicals are well recognised chemical contaminants in the environment and are subject to regulation, monitored in the environment, and are considered to be chemicals of concern.

5.5.1 Release of additives from degrading plastics

Except for some specific reactive organic additives that are chemically bonded with plastic molecules and are integrated into the polymer chain during manufacture, all other additives in plastics are either weakly bound or not bound at all to the polymer molecules. These weakly or unbound chemicals can migrate through the body of the polymer structure to its surface. The migration of additives within and from plastic is a mass diffusion process and the rate of migration of additives from plastic is dependent upon the properties of both the polymer, additive, and environmental conditions.

As biodegradable and oxo-degradable plastics are broken down by abiotic oxidation and biodegradation processes their surfaces become eroded and pitted, and they fragment into ever smaller pieces. These processes increase the effective surface area of the polymer and this continues to increase as the polymeric structure continues to degrade by delamination and breaking of chemical bonds within the polymeric chains. At a molecular level this means the distance a chemical additive needs to diffuse or migrate through to reach the surface of the polymer reduces as the polymer degrades, and there is an expanding surface for them to migrate to, and from.

Therefore, as biodegradable and oxo-degradable plastics degrade in the environment they will release increasing quantities of the chemical additives contained within their polymer structure. Some of these additives will be degraded by the same abiotic oxidation and biodegradation processes that degrade the sub-polymer units (<3000 MW) produced from the parent polymer. Others will be partially degraded and/or transformed by microorganisms to produce potentially persistent and toxic by-products. For example, microbial degradation of two plasticisers commonly used as additives in plastic, di(ethylhexyl)phthalate and di(ethylhexyl)adipate, is often incomplete and significant amounts of the toxic metabolites 2-ethylhexanoic acid and 2-ethylhexanol are formed (Horn et al, 2004).

Other types of additives that are resistant to abiotic and/or biotic degradation will persist and accumulate on the surface of the degrading polymer, from which they can subsequently migrate or transfer into the wider environment. It is conceivable that the rapid degradation of biodegradable or oxo-degradable plastics containing chemically stable additives could produce a pulse of released chemical additives into the surrounding environment. Similarly, residues of biodegradable or oxo-

degradable plastics could provide a significant reservoir or source of such additives within the environments they accumulate and persist within.

There is no readily available data on the types and quantities of chemical additives that are present in biodegradable and oxo-degradable plastics. There are also no reports of studies characterising which chemical additives may be released from biodegradable or oxo-degradable plastics as they degrade and biodegrade, their subsequent persistence once released from the parent polymers, their potential impact on organisms exposed to them, or the impact upon organisms ingesting fragments and MPs containing residues of additive chemicals.

Useful insight into the potential for chemical additives to migrate and be released from plastics can be obtained from food science studies assessing the chemical migration from plastics into food they are in contact with. These studies demonstrate the propensity of numerous classes of chemical additives to migrate from the parent plastic product into food, including the metal lead, tin and cadmium, anti-oxidants, bisphenols, brominated flame retardants, light stabilisers, nonylphenols, phthalate esters, formaldehyde and metaldehyde, methyl tert-butyl ether, benzene, and numerous other volatile organic chemicals, and monomers and oligomers of polymers (Hahladakis et al, 2018).

Furthermore, the parent additive chemicals within plastic polymers can degrade when exposed to light or heat during manufacture, sterilisation, use, and in the environment, to produce transformation products, or non-intentionally added substances (NIAS) within plastic. For example, degradation of the widely used anti-oxidants Irganox 1010 and Irgafos 168 produces a range of smaller sized polar NIAS, including 2,4-ditertbutylphenol, 2,6-ditertbutyl-p-benzoquinone, 3,5-ditertbutyl-4-hydroxyphenylpropionic acid, 2,6-ditertbutyl-4-methoxyphenol, 3,5-ditertbutyl-4-hydroxybenzoic acid, triphenyl phosphate, tri-o-tolyl phosphate, diphenyl phosphate, and 3-(3,5-ditert-butyl-4-hydroxybenzyl)propionic acid. The degradation and transformation of parent chemical additives can produce more toxic or biologically active chemicals. For example, oxidation of tris(nonylphenyl)phosphite, an antioxidant used in PVC and polyolefin polymers, produces the biologically active endocrine disrupting chemicals nonylphenol and octylphenol (Nerin et al, 2013).

NIAS formed by the degradation of additives are often smaller than the original parent chemical and therefore exhibit higher diffusion rates and migration potential from plastic than the parent additives they are produced from. Other factors influencing the rate of migration of chemicals from plastic include the initial concentration of the chemical in the plastic, and the thickness, crystallinity, and surface characteristics of the polymer (Hansen et al, 2013).

The migration of chemical additives from plastic into food involves four major steps which are analogous to those that occur when a chemical additive migrates from plastic within receiving environments:

1. diffusion of an additive/chemical through the polymer
2. desorption of an additive/chemical from the polymer surface
3. sorption of an additive/chemical at the plastic-food interface, or, plastic- sediment/organism interface
4. absorption of an additive/chemical into food, or, absorption into an organism

Food safety regulations require the migration of additives and other substances from plastics in food contact experiments to be assessed under “worse case scenarios” using “simulants” representing

different food categories. These simulants include distilled water, acidic aqueous solutions, alcohol solutions (i.e. 15% ethanol) or octanol or oils (for fatty foods), in combination with a range of temperatures and heating methods (boiling, oven heating, microwave cooking). The rate of migration of additives from plastic increases with increasing temperature, proportion of organic solvent in simulant solutions, and fat content. Aqueous simulant solutions used in food contact assessments can provide a surrogate for the partitioning of additives/chemicals migrating from plastics into freshwater or seawater, or into soil or sediment pore water. Organic co-solvent solutions, octanol, or oils used as simulants can be used to provide a surrogate for the partitioning and uptake of additives/chemicals from plastics into biota.

If an organism ingests plastic fragments or MPs any additives migrating from them will partition into the digestive gut fluids and be absorbed via the intestine. The desorption of additives from ingested plastics and MPs in the gut of organisms is enhanced by surface active substances in gut fluids and the presence of lipids and fats. The action of digestive enzymes upon ingested plastic fragments and MPs within the stomach and gut of organisms that ingest them has not been investigated. If digestive enzymes degrade plastic polymers within the stomach and gut of organisms it is possible this will increase both the rate and extent of migration of chemical additives, and significantly increase the exposure and risk of organisms to them.

These significant knowledge gaps about the potential impacts of biodegradable and oxo-degradable plastic residues and chemical additives they contain in the environment present a significant risk to the health of ecosystems in which these plastics accumulate and persist within. In the absence of research addressing these knowledge deficiencies and the increasing production and use of oxo-degradable and biodegradable plastics the long-term environmental risks of these plastics will continue to grow.

Microorganisms able to biodegrade PHA-type plastics are ubiquitous in the environment, PHA-type plastics biodegrade relatively rapidly in the environment and during composting, and they do not form persistent or toxic products.

The high temperature and moisture content required to degrade PLA plastics are rarely reached in the environment and microorganisms able to biodegrade PLA plastics are relatively scarce.

The biodegradation of PLA plastics under normal environmental conditions is limited and PLA plastic will accumulate in the environment.

The primary mechanism for the degradation of oxo-degradable PE plastic is disintegration and fragmentation, and not biodegradation. The biodegradation of oxo-degradable PE plastics under optimised industrial composting and real-world environmental conditions is limited and oxo-degradable plastics should not be described as being compostable or biodegradable.

The fate and impacts of microplastics produced from the disintegration of oxo-degradable plastics in the environments is currently unknown and represents a significant knowledge gap with respect to their potential environmental risk.

Some biodegradable and oxo-degradable PE plastics may contain chemical additives and other non-intentionally added substances that are released from them as they degrade, some of which are known to be toxic.

6. ECOTOXICITY ASSESSMENTS OF BIODEGRADABLE AND OXO-DEGRADABLE PLASTICS AND THEIR DEGRADATION PRODUCTS

Standards developed to assess the biodegradability and compostability of plastics recognise the need to ensure the media (soil or compost) remaining at the end of such processes is suitable for reuse. In practice this means it retains beneficial properties and has no demonstrable negative properties.

The impact of plastic residue in the environment is related to the time it takes for the polymer to breakdown completely. During every stage of this breakdown process there is the potential for the plastic breakdown products to exert an impact, either as a large object, micro- or nano-sized particle, as a macromolecular, oligomeric or monomeric polymer subunit, or by the release of chemical additives. Therefore, it is necessary to test the toxicity of the final material produced by the biodegradation of plastics.

The standards developed to characterise the biodegradation of plastic materials require the ecotoxicity of the final product to be assessed to ensure that any residual polymer and/or chemical(s) remaining after biodegradation are non-toxic and are environmentally safe. In practice this requirement mainly applies to plastic materials that have been biodegraded by composting processes as the compost product is widely used to raise plants in commercial plant nurseries and added to agricultural soils used to produce food crops.

Standards assessing the compostability of plastics such as EN 13432 require the resulting compost to undergo ecotoxicity assessment to demonstrate it retains no residual toxicity. The ecotoxicity assessment is derived from OECD 208 Guidelines for testing of chemicals (OECD, 2006) and is based on a plant germination and growth assay using a monocotyledon and a dicotyledon plant species. This plant based ecotoxicity bioassay can similarly be used to test for residual toxicity following soil biodegradability assessments of plastic materials.

Other species and ecotoxicity tests used to assess residual toxicity in soil and/or compost following plastic biodegradability tests include earthworms as a representative soil organism (OECD, 2004) and *Daphnia magna* as a representative aquatic organism (OECD, 2012). Earthworms are sensitive to some toxicants, particularly metals, and since they feed on soil they are suitable for testing residual toxicity in soil or compost used for assessing the biodegradation of plastic. The *Daphnia* toxicity test is carried out using an aqueous extract prepared from soil or compost and is used to measure the toxicity of water soluble degradation residues and establish if they are likely to present a risk to aquatic ecosystems. Similarly, an algae growth inhibition toxicity test can be applied (OECD, 2011). Tests utilising microbes that are active in transforming soil nutrients (carbon and nitrogen) have been applied to assess residual toxicity in soil or compost following plastic biodegradability tests (OECD, 2000a&b). Other popular microbial toxicity tests include the standardised luminescent bacteria test (ISO 11348-3, 2007) and Flash test that assess the toxicity of aqueous extracts prepared from test soil or compost.

Very few studies report assessments of residual toxicity in soil and/or compost used to evaluate the biodegradation of biodegradable and oxo-degradable plastics, and those that have reported no measureable toxicological impact. For example, PLA polymer biodegraded by composting generated no toxicity when tested by the luminescent bacterial Flash test and plant growth assays (Tuominen et al, 2002). The degradation of polymers comprised of blends of PHB, PLA and PLLA in soil showed an absence of toxicity as determined by plant toxicity tests (Rychter et al, 2006).

Similar results have been obtained from the degradation of oxo-degradable PE plastics. The degradation of LLDPE agricultural mulch film containing ENVIROCARE additives in soil (Raninger et al, 2002), and the degradation of Environmental Products Inc TDPA-based PE compost bags (Bonora & De Corte, 2003) and oxo-degradable PE film (Guilbert et al, 2005) by composting did not produce toxic products as determined by earthworm, Daphnia, plant, and, bacterial luminescence toxicity tests.

The conclusion of these toxicity tests is that the final products resulting from the biodegradation of biodegradable PHA and PLA based plastics, and oxo-degradable plastics, do not contain any residual toxic components and are environmentally safe. However, as discussed below this conclusion should be treated with caution.

It is important to understand the origins of the standardised toxicity tests that are commonly applied to assess the toxicity of residues from the biodegradation of plastics. Earthworm toxicity tests were designed to assess the impact of persistent bioaccumulative and toxic (PBT) heavy metals and industrial organic contaminants in soil from contaminated industrial sites. Earthworm toxicity tests have subsequently been refined and applied to assess the toxicity of many other substances including agrichemical residues in soil. Plant-based toxicity tests were initially developed to test the efficacy of new agrichemical herbicides. They were subsequently adopted to demonstrate that residues produced by the use, degradation, and transformation of agrichemical herbicides would not cause harm to non-target plant species. Plant-based toxicity tests were adopted to test the potential phytotoxicity of compost after it was found composting did not biodegrade all herbicide residues in plant feed materials, concentrated metal residues, and organic acids persisting from the incomplete biodegradation of organic matter stunted developing shoots and roots of plants. The Daphnia toxicity test was initially developed to assess acute toxicity of industrial effluents and has subsequently been adopted as a standard aquatic organism for ecotoxicity testing in all types of aqueous samples. Luminescent microbial toxicity assays were initially developed as an alternative to more rapidly assess the acute toxicity of industrial effluents.

While these toxicity tests have been modified over time to provide measures of chronic toxicity it is important to acknowledge they were not specifically designed to measure the toxicity of the broad range of substances produced from the degradation and biodegradation of plastics. They have been adopted for this purpose because they were the only standardised toxicity testing protocols that were available at the time. The application of these toxicity tests for assessing potential toxicological impact resulting from the degradation and biodegradation of plastics has limitations that need to be carefully considered when interpreting test results.

Daphnia and luminescent bacterial assays are used to assess the toxicity of aqueous extracts of soil and compost. An aqueous extraction will only recover highly water soluble toxic components from soil or compost samples, will exclude hydrophobic contaminants, and only partially extract

contaminants of mid-polarity. For example, only 10% of 4,4-diamino diphenyl methane (MDA), a mid-polarity toxic degradation product of polyurethane (PU), was recoverable from compost following the biodegradation of PU, whereas quantitative recovery was obtained from a vermiculite matrix (Degli-Innocenti et al, 2001). This highlights the difficulty in extracting and identifying toxic degradation products in complex sample materials like compost.

Luminescent bacterial assays are popular due to the speed in which samples can be prepared and the test completed. This includes the primary extraction of solid samples which usually involves a single aqueous extraction completed within 5-10 minutes. Such conditions are insufficient for extracting hydrophobic organic chemicals from soil or compost including many of the organic chemical additives that can be present in biodegradable and oxo-degradable plastics.

As previously discussed the degradation of PE and other polyolefin polymers used in oxo-degradable plastics produces a range of degradation products including reduced molecular weight polymer units, oligomers, dimers etc. These substances will have little or no solubility in water, will be poorly extracted by aqueous solutions under commonly employed extraction conditions, and will therefore remain in the soil or compost sample.

With plant-based bioassays the germinating and developing plants can only respond to those substances that are able to partition and migrate from the matrix being tested into soil pore water to be bioavailable to the plant. The absence of a toxic response from these toxicity tests does not mean the tested soil or compost does not contain toxic components, nor do they prove that toxic substances will not be released from them in future. A major limitation of current plant-based toxicity tests is their focus on seedling emergence which can have very specific requirements- it has been frequently reported that chemicals having no effect on germination subsequently affect plant growth at later developmental stages (Martin-Closas et al, 2014).

Similarly, the current tests assessing the potential toxicological impact of residues from the biodegradation of plastic upon soil microorganisms are very specific and do not consider broader impacts upon the viability and health of the soil microbiome. For example, the growth and productivity of numerous plants and crops is dependent upon symbiotic and beneficial plant-soil microorganism interactions, particularly with respect to the availability and supply of nutrients within their root zone.

The current standards for assessing the compostability and biodegradation of biodegradable and oxo-degradable plastics do not address the potential effects of residual accumulated plastic residues on soil-dwelling microflora and fauna, and on soil physical and chemical properties (Brodhagen et al, 2017).

Other soil microbial analyses that can be applied to assess the impact of biodegradable and oxo-degradable plastics on soil microbial activity and function include measurements of basal microbial respiration, microbial biomass carbon, and soil enzyme activities (Horswell et al, 2014; Li et al, 2014). Recently, applied polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) and phylogenetic analysis has been applied to demonstrate the degradation of PBAT in soil did not significantly affect soil bacteria but drastically reduced the diversity of fungal flora in the vicinity of the PBAT film surface and reduced the growth of specific fungal species in bulk soil (Moroi et al, 2016). Because fungi play such an important role in the humification process and nutrient cycling in

soil it's crucial to identify and understand both the short and long-term impacts of biodegradable and oxo-degradable plastics upon the soil microbiome.

Considerable quantities of biodegradable and oxo-degradable plastics and their residues are accumulating in soil worldwide, and particularly in productive agricultural soils that humans rely upon to produce food crops. As demonstrated in China, the widespread adoption of using plastic film and mulches to increase crop and food production, without first considering and assessing potential negative impacts, can have serious consequences. In China these include reduced crop yields and widespread contamination of agricultural soils and food crops by plasticisers (Changrong et al, 2014; Liu et al, 2014).

Based on evidence indicating the widespread presence of plastics in all compartments of the environment, it is highly likely that organisms in terrestrial and freshwater ecosystems will come into direct contact with MPs derived from oxo-degradable plastics. The general absence of research reporting the potential ingestion and bioaccumulation of oxo-degradable plastic residues and MPs by earthworms, insects and animals represents a significant gap in our knowledge regarding their possible fate and impact in terrestrial ecosystems. However, the demonstrated consumption and accumulation of MPs by phyla in freshwater and marine ecosystems (nematodes, arthropods, gastropods) that are also common to terrestrial ecosystems suggests similar findings of ingestion, accumulation, and impact of MPs in terrestrial species is inevitable (Horton et al, 2017). These species play an important role in plant decomposition and nutrient cycling so their accumulation of MPs could potentially disrupt these critical ecosystem services. Research in marine ecosystems has demonstrated the accumulation of MPs in a wide range of species at different organisational levels, and their subsequent trophic transfer (Farrell and Nelson, 2013; Watts et al., 2014). Similarly, trophic transfer of MPs between species is likely to occur in terrestrial ecosystems.

Given the known harm that plastic residue and contaminants released from them produce in the marine environment (Engler, 2012; Jahnke et al, 2017) it is difficult to understand the absence of more rigorous examinations of the long-term impacts of the degradation products of biodegradable and oxo-degradable plastics within terrestrial ecosystems.

Oxo-degradable plastics and the MPs they produce are typically hydrophobic and therefore have the capacity to adsorb and accumulate pesticides and other persistent, bioaccumulative and toxic organic contaminants present in terrestrial environments (Horton et al, 2017). Residues of oxo-degradable plastics are likely to become a source of these toxic contaminants within terrestrial ecosystems, and aquatic ecosystems they are transported into.

Worldwide there is an increasing need to maintain healthy and productive soils to produce food which has led to the increasing use of oxo-degradable plastic in its production. The absence of research assessing the effect of fragments of oxo-degradable plastics and MPs on soil microbes and the long-term health and function of soils provides the opportunity for unintended consequences to be realised before we understand their potential impact.

Perhaps the greatest concern regarding the current accepted toxicity tests is their focus on short term effects or acute toxicity. Current tests for assessing the toxicity of residual material following the degradation of plastics in soil or compost are not appropriate for considering the long-term

impact of residual plastic and/or plastic derived additives on soil microorganisms and fauna, soil chemical and physical properties, or the ability of soil to sustainably grow plants.

In view of the types of residues produced from the biodegradation and degradation of biodegradable and oxo-degradable plastics, their overriding toxicological impact is highly likely to be chronic, rather than acute. Therefore, alternative toxicity tests targeting a wider range of potential chronic toxicity endpoints need to be applied to assess the wider range of potential toxicological impacts. For example, many of the common additives in plastic (bisphenol-A and phthalate ester plasticisers, benzophenone type UV stabilisers, phenolic anti-oxidants) have endocrine disrupting properties but none of the current accepted toxicity tests assess this mode of toxicity. The current preferred toxicity tests also do not target other important modes of chronic toxicity including mutagenicity, genotoxicity, or measures of inflammatory response that could result from earthworms, soil arthropods, and other terrestrial animals ingesting and accumulating small plastic fragments in their gut and/or body tissues.

Another important issue to consider about chronic toxicity is that the impact or effect is often not observed in the immediate exposed organism or animal and instead- appears in subsequent generations. Multi-generational toxicity is commonly observed in organisms exposed to endocrine disrupting or genotoxic chemicals where their impact is only evidenced by developmental and/or reproductive abnormalities one or two generations following exposure.

It is timely to consider incorporating a wider range of chronic toxicity endpoints that will provide a more expansive assessment of the potential chronic toxicological impacts produced by the degradation products of plastics in aquatic and terrestrial ecosystems. In-vivo bioassay screening approaches are widely implemented for assessing the toxicity and impact of chemical residues in composted sewage sludge (Kapanen et al, 2013), waste water, and aquatic ecosystems (Boehler et al, 2017; Leusch et al, 2017) and can be modified for application in terrestrial environments. Bioassay analyses combining effect driven analysis (EDA) approaches are already being applied for the hazard assessment of additives, emerging contaminants and NIAS in food contact materials (Bach et al, 2014; Rosenmai et al, 2017; Severin et al, 2017).

Similarly, in-vitro animal model tests using earthworms and terrestrial insects (springtails) combined with transcriptomics are identifying stress response genes and biomarkers of chronic impact resulting from exposure to chemical residues in terrestrial ecosystems (de Boer et al, 2015; Gong & Perkins, 2016). Application of these approaches to assess an expanded range of the potential chronic toxicological impacts of plastic degradation/biodegradation products in terrestrial ecosystems will produce more robust and meaningful assessments of the potential short and long-term environmental risks associated with the use of oxo-degradable and biodegradable plastics.

Standards assessing the biodegradability and compostability of plastics require the final material to be non-toxic.

Very few studies have reported assessing residual toxicity in soil or compost following the biodegradation of biodegradable and oxo-degradable plastics but those that have done so reported no residual toxicity.

Current accepted toxicity tests were not specifically designed to assess the toxicity of the broad range of substances that can be produced from the degradation and biodegradation of plastics.

Alternative toxicity tests that target a broader range of chronic toxicity endpoints including endocrine disruption, mutagenicity, genotoxicity and inflammatory response are required.

7. SUMMARY AND CONCLUSIONS

The focus of this report is to summarise the major classes of biodegradable and oxo-degradable plastics, the methods used to assess their biodegradability and the extent to which they biodegrade, the products and chemicals produced as they biodegrade, and their toxicity and environmental impact.

There is considerable debate about the extent to which oxo-degradable and biodegradable plastics, really do degrade in the environment. In part this results from the use of confusing and often poorly applied terminology, especially with respect to the degradation and biodegradation of oxo-degradable plastics.

While oxo-degradable plastics are often described as being degradable they are not compostable nor fully biodegradable. As demonstrated in numerous studies, residues of these types of plastic will accumulate and persist in receiving environments as fragments and MPs for decades.

Regardless, the number of plastic materials and products manufactured and marketed as being oxo-degradable or oxo-biodegradable is increasing, and manufacturers continue to make claims their products provide improved environmental outcomes. The terms used by producers to market oxo-degradable or oxo-biodegradable plastics, are often insufficiently described, leading to confusion and/or misunderstanding by consumers. Many plastics claiming to be biodegradable are instead bioerodable, hydro-biodegradable, photodegradable, and only partially biodegradable.

Numerous standards are available to assess and validate the rate and extent of degradability and biodegradability of oxo-degradable and biodegradable plastics. The conditions specified in standards for the biodegradation of plastics under industrial composting processes are only achievable within modern well run industrial and municipal composting facilities and will never be achieved within household composting systems or municipal landfills. Similarly, oxo-degradable plastics do not biodegrade in the environment, and some types of biodegradable plastics could persist for years in the environment before being fully biodegraded. Consequently, there is increasing demand from consumers and regulators for new standards that assess the biodegradability of plastics under real-world conditions encountered in terrestrial and aquatic environments.

Consumers would benefit from improved labelling of oxo-degradable and biodegradable plastics detailing the standard specification that was applied to determine biodegradability, the timeframe required and level of biodegradation achieved, and the environmental conditions required to achieve claims of biodegradability.

It is clear biodegradable plastics produced from bio-based polyhydroxyalkanoate type polymers (PHB and PHBV polymers) and PLA polymers are biodegraded during composting. However, while PHB and PHBV biodegradable plastics are biodegraded in aquatic and terrestrial environments within several weeks to months, PLA-based biodegradable plastics will persist for considerably longer periods of time and accumulate in certain environments.

The lack of knowledge of the role of microorganisms and the enzymes they produce on the biodegradation of PE and PP is limiting current understanding of biodegradation mechanisms of PE oxo-degradable plastics. This represents a significant knowledge gap that is hindering the ability to produce oxo-degradable plastics that can biodegrade under real-world conditions in the environments they accumulate and persist within.

Studies reporting biodegradation of oxo-degradable PE plastics in soil or compost have almost exclusively used oxo-degradable PE that has been pre-exposed to UV light and heat conditions that have no relevance to those prevailing in environments they will be used in, or ultimately accumulate within. It is unclear how this common practise of accelerated oxidation prior to biodegradation assessments corresponds to or can be correlated with real-world environmental conditions. The few studies that have assessed the biodegradation of oxo-degradable PE plastics previously exposed to natural temperatures and light levels demonstrate they largely remain intact in soil and sediment and are resistant to biodegradation.

The primary degradation process for oxo-degradable plastics is abiotic oxidative degradation and they do not so much degrade, as fragment into ever smaller pieces of plastic residue, ultimately forming microplastic residues. Therefore oxo-degradable plastics cannot be described as biodegradable or environmentally degradable.

The degradation and biodegradation of oxo-degradable and biodegradable plastics produces a wide range of transformation and degradation products, and other chemical substances that could present a risk in the environment. The oligomers, dimers, monomers and other chemicals produced by the degradation and biodegradation of PHB and PHBV polymers are not toxic and are rapidly biodegraded by microorganisms in receiving environments. Similarly, those produced from PLA are readily biodegraded by microorganisms and no toxic by-products have been identified.

In contrast few studies have investigated the chemicals produced from the degradation or biodegradation of oxo-degradable polyolefin plastics, or their potential fate and impact in receiving environments.

To date there are no studies attempting to quantify the formation or impact of MPs produced from the degradation and fragmentation of oxo-degradable plastics in compost or soil, despite the standards allowing a proportion of plastic residues < 2mm size to remain after biodegradation. Based on the evidence presented in this report it is highly likely that PE-based oxo-degradable plastics will be a significant source of MPs within the environment. If investigated in detail, it is entirely plausible that these MPs will be found to be as equally pervasive in the terrestrial environment as they have been found to be in freshwater and marine environments.

All plastics including oxo-degradable and biodegradable plastics contain chemical additives, most of which are not chemically bound in plastic polymers and are therefore able to migrate from plastic

into the environment. No evidence of toxicological impact of additives in oxo-degradable or biodegradable plastics was found in the summarised literature. However, and importantly, there is an absence of studies reporting the types and quantities of chemical additives present in biodegradable and oxo-degradable plastics, if they release chemical additives as they degrade and/or biodegrade, and their potential impact on organisms exposed to them. The absence of such studies represents a significant gap in our knowledge of the fate and potential impact of biodegradable and oxo-degradable plastics in the environment.

Robust assessments of the potential long-term impacts of residues from biodegradable and oxo-degradable plastic and the additives they contain in soil and terrestrial ecosystems is long overdue and should be a primary focus of future research activities. This is especially relevant in New Zealand where our economy is dependent upon the sustainability of our land-based productive sector.

The general lack of knowledge of the potential impacts of residues of oxo-degradable and biodegradable plastics in the environment is compounded by the limitations of current accepted ecotoxicity test methods. These tests were not specifically designed to measure the toxicity of the broad range of substances and chronic toxicity endpoints produced from the degradation and biodegradation of plastics. In particular, they do not address the potential effects of residual accumulated plastic residues on soil-dwelling microflora and fauna, on soil physical and chemical properties, or the ability of soil to sustainably grow plants.

Much can be learnt from the application of refined and robust strategies that have been developed to better assess the toxicological risks and impact of emerging organic contaminants in the aquatic environment. The use of in-vivo bioassay screening and in-vitro animal model tests combined with transcriptomics are likely to revolutionise our understanding of the environmental impacts and risks resulting from the accumulation, degradation and biodegradation of oxo-degradable and biodegradable plastics in the environment.

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