An overview of degradable and biodegradable polyolefins

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Abstract

The use of engineering plastics, especially polyolefins has increased significantly in recent decades due largely to their low cost, good mechanical properties and light weight. However, this increase in usage has also created many challenges associated with disposal and their impact on the environment. This is because polyolefins do not easily degrade in the natural environment and hence the need for degradable polyolefins has become a major topic of research. Degradable polyolefins are designed to retain
functionality as a commodity plastic for the required service life but degrade to non-toxic end products in a disposal environment. They are typically designed to oxo-degrade while undergoing changes in chemical structure as a result of oxidation in air, thus causing the breakdown of the molecules into small fragments that are then bioassimilated. This article presents (i) a comprehensive review of the chemistry of additives for degradation of polyolefins, (ii) a patent and scientific literature summary of technologies including commercially available systems, (iii) the mechanisms of degradation and biodegradation, (iv) testing methods and (v) toxicity.

**Keywords**

Oxo-biodegradation; degradable polyolefins; biodegradable polyolefins; prodegradants; photodegradation.

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1. Introduction

Products made from plastics, especially polyolefins, have increased significantly in recent decades due largely to their low cost, good mechanical properties, light weight and durability. These properties that make plastics the material of choice for many applications, particularly for single use packaging, together with an increase in usage has also created disposal problems at the end of the useful life of these products. Traditional disposal methods include recycling, incineration and burying in landfill. Since polyolefins do not easily degrade in the natural environment, the need for degradable polyolefins has become a major topic of research in order to manage such environmental problems. The aim of degradable polyolefin design is to retain functionality as a commodity plastic for the required service life but degrade to non-toxic end products in a disposal environment.

Degradable polyolefin systems are typically designed to oxo-degrade undergoing changes in chemical structure as a result of oxidation in air, causing the breakdown of the molecules into small fragments that are then bioassimilated. This article reviews the chemistry of additives used for degradation of polyolefins and presents a summary of technologies including commercially available systems. The mechanisms of degradation and biodegradation, and testing methods are also discussed.

2. Oxo-biodegradation

The term oxo-biodegradation is used to describe the two-stage process of polyolefin degradation. The first stage involves the reaction of oxygen in the air with the polymer. The carbon backbone of the polymer is oxidized
resulting in the formation of smaller molecular fragments. The first stage of oxo-degradation is an abiotic process. The incorporation of oxygen into the carbon chain polymer backbone results in the formation of functional groups such as carboxylic or hydro-carboxylic acids, esters as well as aldehydes and alcohols. The hydrocarbon polymers change their behaviour from hydrophobic to hydrophilic thereby allowing the fragmented polymer to absorb water.

The second stage is biodegradation of the oxidation products by microorganisms (bacteria, fungi and algae) that consume the oxidized carbon backbone fragments to form $\text{CO}_2$, $\text{H}_2\text{O}$ and biomass.

In the first stage of oxo-biodegradation, the oxidative degradation of the polymer can be accelerated by ultraviolet (UV) light (photodegradation) or by thermal degradation using heat over time. Initial abiotic oxidation is an important stage as it determines the rate of the entire process. These processes are described in more detail below.

2.1. Photodegradation

Photodegradation involves the natural tendency for most polymers to undergo a gradual reaction with atmospheric oxygen in the presence of light. Typically a photosensitizing agent is employed to accelerate this natural tendency. The mechanism of photodegradation involves the absorption of UV light which then leads to the generation of free radicals. An auto-oxidation process then occurs which leads to the eventual disintegration of the plastic.

It is believed that the instability of polyolefins is brought about by the presence of impurities (such as carbonyl and hydroperoxide groups) that form during the fabrication or processing of the polyolefin products.
Figure 1 illustrates some of the products formed as a result of photodegradation of polyethylene.[1] The hydroperoxide group (-CH-OOH) is the primary oxidation product and is both thermally and photolytically unstable. It decomposes to produce two radicals, each of which can participate in a chain reaction process. The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and also means that the material is vulnerable to further degradation since these groups are photolabile.

In addition to polymer oxidation initiated by the photolysis of hydroperoxide groups a second major contributor to the photodegradation of polymers is ketone photolysis which proceeds through two major reactions called Norrish I (free radical generation and no chain cleavage) and Norrish II (chain cleavage), as shown below in Figure 2. Ketones are introduced onto the polymer backbone by photo-oxidation and then on further exposure to light these groups absorb photons of appropriate energy, break carbon-carbon bonds and scission the polymer backbone into smaller fragments.[2]

2.2. Thermal degradation

The mechanism and products from oxidation initiated by heat are similar to those resulting from photo-oxidation as represented in Figure 1. One difference between oxidation initiated by heat and by light is that ketone products are stable to heat but not to light.[1] The rate of thermal degradation directly depends upon the temperature, with higher values achievable at higher temperatures.[3] This is discussed in more detail in section 7.2.
2.3. Comparison of polyolefin oxidation

With both photo and thermal degradation of polyolefins, the resistance to oxidation increases with increasing density of the polymer. This is due to a less branched polymer having a diminished permeability to gases and a smaller number of tertiary carbon atoms, which constitute sensitive points of attack.[2, 3] In addition to chain branching, chain defects, such as unsaturation, can also influence the rate of degradation. The oxidation susceptibility of polyolefins can be listed as follows: iPP (isotactic polypropylene) > LDPE (low density polyethylene) > LLDPE (linear low density polyethylene) > HDPE (high density polyethylene).[3] Oxidative degradation in polypropylene leads primarily to chain scission, whereas in polyethylene, during the initial stages cross linking occurs.[4]

2.4. Degradation from Mechanical stress

Although rarely studied (c.f. degradation by UV light and heat), the application of mechanical stress can also accelerate the degradation of polymers. This is because the degradation mechanisms are morphology dependent and stress causes changes in the polymer morphology. The influence of mechanical action alone has been reported to cause degradation, e.g. shear forces in an extruder or mill.[5] The influence of mechanical forces on photodegradation has also been reported with stress shown to accelerate photodegradation.[5]
2.5. Biodegradation

During the microbial degradation stage, most of the abiotic oxidation products (low molecular weight compounds) are utilized by the microbes. An important aspect during this biodegradation stage is the sustained growth of microorganisms. It has been reported that to achieve significant biodegradation in a reasonable time period, the average molecular weight of oxidized polyolefin should be under 5000Da.[6]

A decrease in the number of carbonyl groups occurs during the microbial degradation stage. This consumption of carbonyl groups from the original oxidation products such as ketones, esters and lactones indicates that the microorganisms are growing. Eventually the microorganisms degrade the smaller segments of polyolefin to form carbon dioxide and water as end products.

The mechanism of polyethylene biodegradation has been previously outlined[7] and is discussed in more detail in section 6.

3. Prodegradant Technology

Although polyolefins such as PE and PP will degrade naturally, the time scale is far too long for them to be considered environmentally friendly. Increasing demand for these polymers requires ways of converting them into biodegradable materials in significantly shorter periods of time. The solution lies in accelerating the natural oxidative degradation of the polymers. The use of such prodegradant additives will be reviewed in this section of the review.
3.1. Transition metal salts

3.1.1 Mode of prodegradant activity

Transition metal ions are the most widely reported prodegradant additives currently in use. The attractiveness of these additives lies in their ability to catalyse the decomposition of hydroperoxides into free radicals (Figure 3).[4] The most commonly used transition metals include iron, cobalt and manganese. Iron is highly effective in accelerating photodegradation while manganese and cobalt are sensitive to thermal degradation. The metal ions are generally introduced at trace levels in the form of an organic complex. Specific examples are outlined in the following section.

3.1.2 Transition metal salts of fatty acid esters, amides and dithiocarbamates

One of the earliest patents to claim the use of transition metal ions as prodegradant additives in polyolefins is US3454510 filed in 1966 (assigned to Eastman Kodak).[8] The invention relates to controlled degradation rates of agricultural films and includes the use of additives such as acetyl acetonates of manganese, cobalt, chromium, copper and vanadium, the alkyl acetoacetates and alkyl benzoylacettes of copper, vanadium, chromium, manganese, cobalt, iron, nickel and zinc. Preferred examples of prodegradants also include manganese stearate, manganese oleate, manganese acetate, cobalt acetate, cobalt stearate, cupric oleate and ferric acetate. In addition to the prodegradant additives, the patent describes the use of pigments or dyes, e.g. carbon black, to reduce the transmission of sunlight and hence control the degradation rates.
Another early patent to claim the use of transition metal ions as prodegradant additives in polyolefins is that of Scott, US4121025, filed in 1971.[9] In this patent it was reported that the metal complexes were activated by light (and optionally heat) to accelerate degradation. Once photodegradation had commenced by the action of UV light then rapid oxidative degradation of the plastic continued even if the source of light was removed. The transition metal complexes were still found to act as photoactivators even in polymers containing antioxidants and stabilizers. Iron was reported as the preferred metal ion; however, cobalt, nickel, manganese, silver, palladium, molybdenum, chromium, tungsten and cerium are also mentioned. The patent also reports on synergy if a mixture of zinc and iron is used. Many organic complexing agents can be used to bind the metal ion, provided that the complex is degradable by UV light. The patent gives many examples and claims that sulphur ligands are preferred over nitrogen, oxygen or phosphorus. An example of a sulphur containing complexing anion is dibutylthiocarbamate.

The U.S. patent 5,854,304 (EPI Environmental Products Inc.)[10] discloses the combination of a metal carboxylate and an aliphatic poly hydroxyl-carboxyl acid as prodegradants. The preferred metal carboxylates are cobalt, cerium and iron stearate. The aliphatic poly hydroxyl-carboxyl acid is defined as an aliphatic acid having either more than one hydroxy (-OH) or more than one carboxyl (-COOH) group in the acid structure. Most of the examples in this patent include citric acid (see Figure 4).

The patent WO2008/020752 (assigned to Gain Mark Technology)[11] describes the use of fatty acid amides to improve the rate of degradation of
prodegradant systems containing transition metal ions. The preferred amides contain between 8 and 20 carbon atoms and the example given is oleamide or 9-octadecenamide (see structure below). As well as the transition metal salt (preferably cobalt chloride or cobalt nitrate) and fatty acid amide (oleamide - see Figure 5), the composition also consists of a carboxylic acid (lauric, stearic, palmitic, oleic, linoleic) and a base (sodium hydroxide).

3.1.3 Ferrocene

There are a number of patents that report on the use of ferrocene as a prodegradant. The structure of ferrocene is shown in Figure 6. It consists of two cyclopentadienyl rings bound on opposite sides of a central iron atom. The patent BE816647 (assigned to BASF)[12] dates back to 1974. It describes the use of a carbonyl substituted ferrocene as a prodegradant for polyolefins. Similarly, the patent GB1382061 in 1975 (assigned to ICI)[13] describes the use of ferrocene and/or an alkyl substituted ferrocene and/or a carbonyl substituted ferrocene to increase photodegradation. An amido alkyl substituted ferrocene is reported in CN1090300.[14] The patents DE2331676 (assigned to BASF)[15] and CN101260195[16] also describe the use of ferrocene to accelerate the degradation of polyolefins with CN101260195 disclosing the use of mixtures of ferrocene, cesium stearate and TiO₂. Benzophenone additives have also been reported together with ferrocene in the patents DE2244800[17] and SU626101.[18] The patent WO200259195[19] describes a complex mixture of ferrocene with other metal ions as well as non metallic fillers. It does not mention starch, but instead it discusses the use of chitin and casein. There is also a report of accelerated
photodegradable PE film by gamma radiated PE that contains ferrocene as described in the patent SU592324.[20]

Some of the chemical structures for the metal coordinating anions mentioned in the above examples are shown in Figure 7 to Figure 10.

### 3.1.4 Metal oxides

Metal oxide polymer additives such as TiO$_2$ and ZnO are known UV absorbers and are also often added to impart a white colour. The photostability of the metal oxides is very dependant on surface treatment, particle size and crystalline form. While the UV stabilising effect of ZnO in polyolefins is well recognised[21, 22], the control of photoactivity via introduction of metal ions into the lattice has also been reported.[23, 24] Similarly, the effect of transition metal doped TiO$_2$ on the photodegradation of polyethylene has recently been reported.[25] The rate of photodegradation can be reduced by using coated TiO$_2$ particles or TiO$_2$ doped with Cr or Mn ions. The rate was also shown to increase on adding TiO$_2$ doped with V and Mo or W ions.

European patent EP1696004 describes the use of transition metal coated pigments and fillers as prodegradants.[26] The use of a transition metal coating on fillers such as the anatase or rutile form of titanium dioxide offers improved performance. Other fillers include calcium carbonate, talc and clay. Preferred transition metals include iron and manganese. The process of coating the fillers is described and involves the dispersion of a fatty acid transition metal ion salt and filler in an alcohol solvent followed by a calcination step to obtain the final transition metal oxide coating on the filler. One or more transition metals may be used on the same filler. An example illustrated in the patent is TiO$_2$ coated with FeO and MnO.
The addition of TiO$_2$ with other metal stearate prodegradants has also been reported.[16, 27] A rare earth modified TiO$_2$ photocatalyst is also reported in patent CN101181678.[28]

3.2. **Transition metal free systems**

While the majority of literature on oxo-biodegradation includes transition metal salts, there are also a few reports of other prodegradant additives that do not contain any transition metals.

3.2.1 **Mode of prodegradant activity**

Most commercial polyolefins will undergo chemical modifications under UV light because they contain impurities or additives that possess chromophoric groups. It is these chromophores that will absorb the light or photon of given energy. Photodegradation was described in Section 2.1 of this report and the presence of carbonyl groups was shown to be important in the degradation mechanism. The spectrum of sunlight penetrating the earth’s surface ranges from 290-3000 nm with UV light in the range 295-380 nm. While saturated compounds possessing bonds such as C-C, C-H, O-H will absorb light at wavelengths below 200 nm, both carbonyl groups and conjugated double bonds have absorption maxima between 200 and 300 nm.[2] The deliberate introduction of these groups into the polymer to accelerate the degradation is illustrated in the following sections.
3.2.2 *Ketone copolymers*

Early examples were the use of copolymers which included a carbonyl group alpha to the main chain, known as the Ecolyte™ process.[1][29] Vinyl ketones were copolymerised with the specific vinyl monomers to produce polyolefins having greater sensitivity to sunlight than those containing no ketone groups. Similarly, photosensitive condensation polymers have been synthesised with ethylene-carbon monoxide copolymers (ECO). These have been used for loop carriers for beverage can 6 packs [1] as well as for containers, closures and foodtrays.[30]

3.2.3 *1,2-oxo-hydroxy groups*

Patent WO2008/006492 (assigned to DSM) describes how oxo-biodegradation of polyolefins can be achieved through the addition of additives containing at least one 1,2-oxo-hydroxy-moiety according to the structure below.[31] (Figure 11)

The key point in this patent is that the metal $M^+$ is not a transition metal, but instead, an alkaline earth metal cation or an ammonium ion. Examples of the additives include citric acid and tartaric acid combined with potassium, lithium or sodium carboxylates. Other alkaline or alkaline earth metal salts include those from fatty acids, e.g. stearates, palmitates, linolates and oleates. The patent also describes the addition of stabilizers to control the processability and lifetime of the polymer. The addition of other fillers including starch is also mentioned.
3.2.4 Unsaturated alcohols or esters

US patent 4256851 (assigned to Owens-Illinois)[32] discloses the use of an ethylenically unsaturated alcohol or ester to degrade polyolefins. A carbon hydrogen bond is activated with respect to hydrogen atom abstraction by an adjacent carbon carbon double bond. This facilitates thermal or photooxidation to hydroperoxides and subsequently free radicals. Some examples of alcohol structures listed include geraniol, linalool, citronellol, allyl alcohol and furfuryl alcohol (Figure 12).

Examples of some esters listed include geranyl acetate, linalyl acetate and furfuryl acetate (Figure 13).

The patent WO9015096 (assigned to Techmer)[33] describes similar unsaturated ethylene structures to that described above in US patent 4256851. The additive is described as containing at least one alkoxyalted ethylenically unsaturated or saturated compound as prodegradant. The oxyalkanoyl groups must not be recurring for enhanced photosensitivity. Examples listed include alkoxyalted derivatives of the alcohols geraniol, linalool, citronellol as well as alkoxyalted derivatives of the acids sorbic acid, oleic acid, linoleic acid. The general structure is given as:

\[ R-\text{CO-O-(AO)}_x-\text{H} \]

Where R is an aliphatic radical containing 8-22 carbon atoms and contains a site of ethylenic unsaturation and A is a bivalent radical, preferably \(-\text{CH}_2-\text{CH}_2-\) and \(-\text{CH-}(\text{CH}_3)-\text{CH}_2-\).

Further examples listed in this patent include non-ionic surfactants or dispersants and many commercial examples of these are given in the patent,
e.g. Polysorbate 60. The detailed examples given use ethoxylated castor oil and Polysorbate 60 (Figure 14).

3.2.5 Benzophenones

Benzophenone based additives are known to accelerate the degradation of polymers in the presence of air and UV light. US patent 4038227 describes the use of benzophenone and anthraquinone additives as prodegradants in PE and gives examples of activity both alone and together with other additives such as iron stearate and coloured pigments.[34] The structures are shown in Figure 15. While the additives alone showed some accelerated degradation relative to the neat polymer, systems containing both the benzophenone additive and transition metal stearate were found to be most effective for promoting degradation of polyolefins. Inclusion of certain coloured pigments was found to enhance the prodegradant effect. A brown coloured pigment showed particularly accelerated degradation, presumably due to iron salts present in the pigment.

The Patent US3846395 (assigned to ICI) also discloses the use of benzophenones to degrade polyolefins.[35] In this patent the preferred additives are p-laurylacetophenone and p-laurylbenzophenone (Figure 16).

Benzophenones are also mentioned in the Japanese patent JP48070755[36] where they are used together with transition metal compounds and in the patent WO1992011298[37] which discloses the use of two transition metal compounds, iron and copper stearate and benzophenone. The US patent US4024324 describes the use of aryl ketones together with a borate or
phosphate ester of an alkanolamine for greater control of strength prior to degradation.[38]

3.2.6 γ-Pyrones

US patent 3679777 describes the photodegradation of polyolefins containing γ-pyron ring compounds such as chromone, flavone or xanthone.[39] The degradation rates can be controlled by varying the additive loading. It is interesting to note that these compounds can migrate to the polymer film surface at higher concentrations and they can form a protective UV screening layer. Lower concentrations are preferred for increased polymer degradation. The structures are shown in Figure 17.

3.2.7 β-diketones

The use of β-diketones (or 1,3-diones) as prodegradant additives in polyolefins has been reported in US patent 3994869.[40] The patent describes the synthesis of some aryl substituted additives and gives examples of degradation of these additives in the presence of calcium stearate. The structure is shown in Figure 18 and can also exhibit keto-enol tautomerism.

3.2.8 Polyisobutylene

US4197375 patent (assigned to Chevron) is another example whereby no transition metal prodegradant is used.[41] This patent describes the use of polyisobutylene to improve the rate of photodegradation of polyolefins. Although incorporation into the bulk polymer is briefly mentioned, in the
example given the additive is applied to the surface of a PE film and compared to benzophenone.

### 3.2.9 Selected Amines

Various amine structures have been also reported to act as prodegradants in polyolefins. The patent JP75006219 (assigned to Chisso corp.) describes the use of hexmethylene tetramine (also known as hexamine, Figure 19).

In another patent assigned to the same company (Chisso corp.) JP74035334 it is disclosed that the amine guanidine and/or phenyl naphthyl amine have prodegradant activity.[43] (Figure 20).

The patent US 4360606 (assigned to Owens-Illinois) also describes the use of amines as examples of additives used together with ketones to photodegrade polyolefins. Some examples given contain ethylenic unsaturation, e.g. oleylamine (Figure 21) and linoleylamine, while other examples contain saturated CH₂ bonds, e.g., n-decylamine and spermine.

### 3.2.10 Peroxides

Patent WO2008/037398 (assigned to Clariant) describes the use of a peroxide containing additive for targeted scission or cross linking reactions in plastics.[45] The masterbatch comprises a peroxide (15-85 %) and polyolefin waxes. The peroxide is di-t-butyl peroxide, dicumyl peroxide or diacetyl peroxide.
WO2007/028731 (assigned to Ciba) discusses the preparation of degradable polymers triggered by light and/or heat and/or humidity. The patent gives a great deal of detail on the organic structure of the degradation accelerator and its many variables; however, it also mentions that the preferred composition should also contain transition metal salts, antioxidants and inorganic oxidants such as inorganic peroxides of alkali, alkane earth or transition metals. The inorganic metal peroxide is sensitive to humidity and reacts with water in order to liberate an auxiliary active prodegradant species. Organic peroxides and hydroperoxides are mentioned in the patent US4360606 (assigned to Owens-Illinois) as examples of photosensitizers, effective as prodegradants when used together with other oxidisable additives. The examples include t-butyl hydroperoxide, cumene hydroperoxide, p-methanehydroperoxide, t-butylperoxybenzoate and dicumyl peroxide (Figure 22).

4. Commercially Available Prodegradants

Prodegradants is an old technology that has only been commercially important in recent years. Patents surrounding the science of prodegradant additives and degradable polyolefins have dated as far back as the early 1940’s. The first generation of degradable polyolefins began with incorporation of photo-sensitive unsaturated moieties into the polyolefin backbone in patents dated to 1941 and 1950 to Bayer and Du Pont respectively. Patents surrounding photo-sensitive carbonyl groups through polymerisation of ketones to yield vinyl ketone copolymers came later from Guillet in the early 1970’s, followed by transition metal complex sensitizers.
from Scott et al in 1978[47]. Other more advanced additives based on the early technologies progressed to include a larger range of metal complex sensitizers, blending with other biodegradable constituents and use of prodegradants with stabilisers and antioxidants to tailor the degradation profiles. The following sections cover the popular commercial prodegradant and degradable polymers found in literature to date. Some description of their mechanism, technology claims and compliance with any standards (if any) is given.

4.1 Transition Metal Salts

A large percentage of commercially available prodegradants have been based on transition metals in the forms carboxylates and dithiodicarbamates for mostly polyolefins. Degradable finished products are widely available through many compounders, who have obtained licence rights to use pre-packaged prodegradants from the manufacturers. Some popular prodegradant manufacturers are listed in Table 1.

EPI is one of the key players in the current prodegradant market. EPI manufactures, distributes, sells and licence out their Total Degradable Plastics Additive (TDPA™) to other plastic fabricators to produce oxo-degradable polyolefinic products. Their prodegradants are used in a vast variety of finished products such as carrier and disposable waste bags, food packaging and food service items, “bubble wraps”, personal care products (diapers), and agricultural mulch films.

There are many licensees that use TDPA in many polyolefinic products. The list of some companies is as below:
Agricultural mulch films utilising TDPA prodegradants have been developed and marketed by Ciba Speciality Chemicals under the tradename of Envirocare™ [1].

LDPE bubble wraps and bags has been developed and produced by Sancell under the name of “Enviro Bubble” and “Enviro Protecta Bag”.

Copol International produces degradable cast polypropylene (CPP) films for various non-food contact packaging.

Ecosafe has a range marketed under “Ecosafe 6400” for compostable single use bags.

“Encore” degradable film technology by Command Packaging for shopping bags.

Polynova Industries for degradable shopping bags.

Belcorr Packaging for degradable shopping bags.

Transco Plastic Industries for degradable shopping bags.

Polyolefins containing TDPA is degradable by the action of sunlight as well as been compostable. It can also be recycled before degradation begins. TDPA can be incorporated in a range of polyolefins such as polyethylene (low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (high density polyethylene (HDPE) and combinations), polypropylene (homopolymer and co-polymer), and polystyrene (expanded polystyrene (EPS), general purpose polystyrene (GPPS), high impact polystyrene (HIPS)). It can be processed by conventional methods such as blow moulding, casting, biaxial drawing, injection moulding, extrusion, thermoforming and coatings. Only low levels between 2 to 3 %wt of the additive to the conventional
polyolefin will result in degradation 20 to 36 months when disposed in an appropriate environment.

Renatura is a patented blend of metal pro-oxidant (iron stearate) and antioxidants/UV absorbers sold as a masterbatch for PP and PE. The use of Renatura has been exclusively licensed to Diamant Art Corporation in 2007 to produce biodegradable products under the tradename of “BioSmart” by their subsidiary company, Bio-Plastics Film Inc. The current product line of Diamant Films is plasticiser free PVC shrink wraps.

Only low level loadings of ~2%wt are required to produce degradable polyolefins and are process friendly, such that they can be used in standard production processes (extrusion, casting, blow moulding and injection moulding). It is also recyclable prior to degradation initiation and is compatible in high temperature processing. It is claimed that it has a long shelf-life compared to other prodegradants, made possible through the inclusion of stabilisers.

Reverte is an oxo-biodegradable additive sold as masterbatches for polyolefins (PP, PE) and has claimed to be the first additive for degradable poly(ethylene terephthalate) (PET) for beverage bottles. It is also suited for acrylonitrile-butadiene-styrene copolymers (ABS). For degradable beverage bottles, Planet Green Bottle Corporation, which has alliances with Norland International, has an exclusive agreement with Wells Plastics Limited for all oxo-biodegradable PET preforms and plastic bottles to the beverage and pharmaceutical industries globally[48]. Other common articles with Reverte include carrier bags, checkout bags, rubbish bags, fruit netting, food containers, disposable food utensils, trays and punnets.
AddiFlex was also targeted for finished products such as food packaging and food service items and carrier and waste disposal bags. It is available through Green Club Inc and Omya and there are 2 grades available for food contact applications. It is described as a thermo-oxidative additive system that works in synergy with calcium carbonate (CaCO₃) (patented). The presence of CaCO₃ has the ability to increase UV degradation by up to 66% hence less additive is required. AddiFlex is used in a variety of food packaging manufactured by Active Packaging, Robert Plastics Ltd for LLDPE based films for a variety of consumer products and Jig-A-Loo’s Econogreen product line of plastic bags and drop cloths. It has claimed to be biodegradable to form water, carbon dioxide and biomass.

Symphony Environmental produces pro-degradants that is degradable but not intended for compost under the tradename, d₂W. It is provided as a masterbatch and only 1 to 3%wt is required to produce degradable polymers. It contains metal salts and stabilisers to allow for different lifetimes. There are four grades available and other formulations can be tailored to suit the desired application. It is not intended for compost as it does not degrade in anaerobic conditions. Some consumables utilising d₂W are from Nescafe, Tiger Brands, Barclay, Pizza Hut, KFC, Tesco and Walmart.

The protegradant utilising metal dithiocarbamate (iron and possibly nickel) called Scott-Gilead technology has been used to produce mulch films under the tradename of Plastigone in USA and Plastor in Europe. The metal dithiocarbamate differs from metal carboxylate such that it functions as an
antioxidant during processing and storage. Once exposed to UV light, it behaves as a photo- and thermo-prooxidant.

4.1.1. Technology Claims

TDPA technology utilises a combination of transition metal carboxylate and an aliphatic poly(hydroxyl-carboxyl acid) in a polyolefin [49], as disclosed in US patent 5,854,304. Metal carboxylates are well known to accelerate peroxidation of hydrocarbon polymers [50]. The preferred metal carboxylates are cerium, cobalt and iron stearate. Iron is recognised as photo-initiating where as cobalt (nickel, chromium(IV) and copper) are sensitive to thermal activation [51]. The poly(hydroxy carboxyl acid) described are aliphatic acids with either more than one hydroxyl groups or more than one carboxyl moieties. Citric acid was such acid given in the examples. It was claimed that it is the use of the metal stearate and acid allows degradation to occur in compost (anaerobic conditions and in absence of UV light).

The induction time, which is the time interval that degradation begins, can be tailored to suit the application. The lifetime can range from a few weeks to 2 years. The lifetime or induction time can be modified by the choice of type of metal stearate, acid and their compositions as disclosed in the patent. Further control can be attained by addition of stabilisers such as diphosphonite to increase the induction period. Conversely, additional oxidisers such as iron oxide, manganese dioxide, cerium hydroxide and perchlorates can be included to significantly reduce the induction period.

The degradation profiles of the TDPA technology was demonstrated in a study by Chiellini et al [52] during accelerated thermal oxidation. LDPE films with a
10 to 15 wt% of two different grades of TDPA masterbatch (DCP540 and ZSK 1314) were tested in an oven at 55 and 70 °C and the thermal oxidation behaviour was monitored by changes in the carbonyl indices. Generally, an increase in the carbonyl index (CI) is indicative that degradation to low molecular weight carbonyl compounds is occurring.

In dry conditions, the induction time of DCP540 was 1 to 5 days (depending on the temperature) whereas a much longer induction time of 11 to 32 days was possible with ZSK1314, presumably controlled by the type and/or level of stabiliser. The two grades of TDPA also exhibited different behaviours in wet and dry conditions. In humid environments, DCP540 underwent oxidation at a much reduced rate and displayed longer induction periods whereas the oxidation rates of ZSK1315 were relatively comparable to dry conditions. The rate of oxidation was also accelerated by higher temperatures. Despite the environmental variables, the final extent of oxidation was comparable with different degradation periods.

Biodegradation (i.e. mineralization) of LDPE containing TDPA was further studied in controlled laboratory environments[53]. The samples were initially thermally oxidised to simulate the beginning stages of oxo-biodegradation and then subjected to respirometric (CO₂ evolution) tests in soil and mature compost mediums.

The degree of mineralization during soil burial of two PE containing TDPA was significant (about 50 to 60%) over a period of 18 months. This was comparable to the control, which was filter paper that was essentially composed of cellulose. The rate of biodegradation was noted to be slower.
than the control but the ultimate extent of biodegradation was similar. After 70 weeks, no PE fragments could be retrieved from the soil.

Respirometric aerobic testing in mature compost media (55°C) was also found to display relatively slow rates of mineralization. After incubation for 426 days, mineralization reached 27.8% and was expected to continue to rise from the positive slope of the biodegradation curve.

A complimentary study of biodegradation of thermally oxidised PE films containing TDPA evidenced that bacterium and fungus growth occurred on the surface of the films and colonisation of two bacterium and fungus was quite rapid[54]. Analysis of the film surface detected proteins and polysaccharides, which are associated with microorganism growth rather than oxidation products. The film surface appeared to be pitted and eroded upon removal of the microorganisms (Figure 23).

Renatura solely use iron stearate as a prodegradant in their blend. Iron was chosen over other transition metals as restrictions were less demanding in applications for food contact[55]. Nor-X produces their own iron stearate, as disclosed in their patents WO 2004/094516[55] and WO2006/043827[56]. They claim that their synthetic method produces iron stearates with higher activity and of lighter brown colour compared to those commercially available. This was possible by treatment of iron stearate with 2 to 5% aqueous hydrogen peroxide which is thought to maintain more ferric ions in its highest oxidation state (III). Thus higher catalytic activity is attained and lower proportions of Fe (II) results in a lighter brown colour[55]. Thermoplastics containing iron compounds are usually yellow-brown or dark brown, which may not be desired for cosmetic reasons. Hence the lighter colour obtained
through their synthetic process reduces this effect. The recommended dosage of iron stearate in polyolefins for rapid degradation was greater than 0.03%wt. The other essential components of Renatura are long term stabilisers (non radical forming) to control the time and rates of degradation. Long term stabilisers of interest include UV absorbers, hindered phenols and hindered amines. The adjustable lifetimes of PP-LLDPE containing 0.5% of prodegradant with different types of long term stabiliser is illustrated in Table 2. The samples were subjected to accelerated ageing in a UVCON weather-o-meter in accordance to ISO 4892-3.

UV absorbers are typically benzotriazoles, benzophenones and hydroxyphenyl triazines. They prevent polyolefin degradation by preferentially absorbing UV light instead of contaminant chromophores which prevents chain scission of the polymeric backbone. UV light is then converted to heat via keto-enol tautomerism (Figure 24) to its mesomeric form which is an excited state. It returns to its ground state via heat dissipation and continues to function as a light stabiliser by this cyclic mechanism[57].

However, UV absorbers will eventually be depleted by oxidative degradation and the preventative action against polymer degradation ceases. Thus UV absorbers of high stability to oxidative degradation (such as Tinuvin 1577, Ciba Specialty Chemicals) in combination with iron stearate were found to display longer lifetimes than those of lower stability (Sanduvor PR 25, Ciba Specialty Chemicals). The lifetimes are also dependent on the ratio of prodegradant to UV absorbers as well as their concentrations.
Hindered phenols or phenolic antioxidants are also light stabilisers and can function, by the patent’s definition, as a process stabiliser as well as a long term stabiliser. Hindered phenols are primary antioxidants that behave as hydrogen donors. They react with peroxyl radicals to form hydroperoxides and prevent hydrogen abstraction from the polymer backbone, inhibiting chain scission. The deactivation mechanism of peroxyl radicals (ROO•) by hindered phenols is illustrated in Figure 25.

The phenoxy radical generated is very stable, owing to its ability to resume various mesomeric forms (Figure 26).

Adjustable lifetimes of degradable polyolefins can be obtained through the use of iron stearate and hindered phenols with different stabilities. Similarly to UV absorbers, the use of higher stability hindered phenols resulted in longer lifetimes as oppose to those of lower stability. The stability is determined by the steric size of the substituent in the ortho and para positions to the oxygen bond. Tert-butyl groups in the ortho positions tend to shield the oxygen based radical centre most effectively from reacting further to the more thermodynamically stable non-radical groups. In instances where the ortho substituents are the same, the alkyl group located in the para position becomes the determining moiety in its activity and stability. Hindered amines are by far the most efficient light stabilisers (commonly abbreviated to HALS). They are also proficient as thermal stabilisers. They are derivatives of 2,2,6,6-tetramethyl piperidine and its effectiveness at low
concentrations is due to its cyclic mechanism where HALS is regenerated and not consumed during stabilisation (Figure 27). They do not absorb UV light.

Again, highly stable HALS of high molecular weight was found to result in longer lifetimes than the lower molecular weight HALS of lower stability. Polyolefins utilising high molecular weight HALS, Tinuvin 622 (Ciba Specialty Chemicals) was found to exhibit longer lifetimes than lower molecular weight Tinuvin 770 (Ciba Specialty Chemicals).

For short lifetimes, sole use of process stabilisers can facilitate such requirements. Such process stabilisers include phosphites, hydroquinone compounds and C-H acid radical scavengers. High temperature processing is also possible with the correct choice of high temperature process stabiliser in the Renatura blend.

No other components that directly drive biodegradation were disclosed in their patents. However, biomineralisation was assumed to occur as the additives induce polyolefins to a state that readily allows micro-organisms to biodegrade the fragments (of low molecular weight below 5000 g/mol). In compost environments, UV light is absent and only heat is available to further drive degradation. Even though iron stearate was recognised as highly photosensitive and exhibit poor thermal sensitivity, a study has shown that degradable PE and PP with 2%wt Renatura continued thermal oxidation in absence of light continued after photo-oxidation had occurred[51]. Compost environment conditions were simulated by initial exposure to UV light in a UVCON unit (according to ISO 4892-3 or ASTM G154) followed by exposure to heat for defined periods in an oven at 70 °C (in absence of light). The
elongation at break, which was indicative of the degree of degradation, was found to sharply reduce, especially with longer initial exposure to UV light. The findings of this study deduced that although the additives did not directly drive biomineralisation, continued thermal oxidation in presence of oxygen but absence of light, as in landfills, provided the appropriate states of the polyolefin to undergo biomineralisation.

No patents could be found assigned to Wells Plastic Limited for their proprietary oxo-biodegradable additives, Reverte. However, it has been disclosed that Reverte consist of three main components:

1. A photo-inhibiting package to protect the product before disposal.
2. A metal ion prodegradant package to control the chain scission phase during degradation.
3. Secondary biodegradation promoters to initiate and enhance biodegradation rates.

The control of lifetime or induction time of the degradable products containing Reverte before disposal is controlled by a package of non-disclosed stabiliser and/or antioxidants (radical scavengers). The stabilisers and/or antioxidants were described as very efficient free radical scavengers which break down into less efficient free radical scavengers once exposed to a very small amount of UV light. The stabilisers are eventually consumed, which allows oxidation of the polymers to take place.

The metal prodegradant is assumed to include either common stearates of iron, cobalt, and/or manganese to catalyse chain scission of the polymeric backbones. The secondary biodegradation promoters have been disclosed to include microcellulose powder, which readily biodegrades.
Reverte additives has claimed to be photolytically and thermally activated. In-house experiments have proven that in the absence of light, thermo-oxidation readily occurs and the time to reach embrittlement was highly dependent on the exposure temperature (and Reverte loading).[58]

Films of HDPE, LDPE and cast and biaxially orientated PP containing Reverte were shown to exhibit rapid rates of degradation under UV light (with UVA 340 lamp at 50 °C). The rate of degradation was determined by the carbonyl index, CI.[59] Generally a higher level from 1 %wt to 5%wt of additive can dramatically accelerate the period to reach the embrittlement stage.

Biodegradation proceeds usually after fragmentation, which is accompanied by a decline in molecular weight to 10,000 or below. Microbial degradation of polyolefins containing Reverte was proven in their in-house laboratory tests (Figure 28).

It has been disclosed that Reverte formulations contained micronized cellulose, which can contribute to a faster rate of mineralisation of the overall film. LDPE films with Reverte additive displayed significant biodegradation when incubated for 5 weeks in a bacterium (Figure 28(b)) where as the virgin LDPE film did not show any visible signs of biodegradation (Figure 28(a)). On closer inspection, bacteria growth throughout the LDPE film with Reverte was observed (Figure 28(c)). Utilising SEM, cracks within the film and significant bacteria formed a biofilm on the film surface were observed (Figure 28(d)).

Further confirmation of biodegradation was evidenced in laboratory compost tests utilising oxygenated compost columns. The tests maintained at 50 °C of PE films after fragmentation evidenced that 60%wt mineralisation of PE films
was reached after 400 days. Thermoformed PP films with Reverte after fragmentation were tested in the compost columns at 60 °C and showed that 60% mineralisation was achieved after approximately 700 days. The different times achieved between PP and PE samples were attributed to the initial sample thickness.

AddiFlex additives has been disclosed as a multicomponent system of iron and/or manganese stearate, calcium carbonate, starch (particularly from corn) and/or cellulose fibres[60]. The grade AddiFlex HE has been identified to contain manganese stearate[61]. It was proposed that calcium carbonate acted as a synergist to the metal stearate to enhance the degradation rate, thus less additive is required. In a particular study, testing with SEPAP weatherometer followed by oven aging showed samples with CaCO₃ had a significantly higher carbonyl absorption (FTIR) than that without at the same pro-oxidant loading. Furthermore, the presence of CaCO₃ did not modify the stoichiometry of hydroxylated and carboxylated groups formed. Further evidence of the increased rate of degradation in the presence of CaCO₃ was observed in an oven aging test, followed by mechanical testing to quantify the degree of decomposition. At a pro-oxidant loading of 3%wt, the presence of 10%wt of CaCO₃ vastly reduced the elongation at break from 198% to 75% after aging at 80°C for 8 days. A higher loading of 7%wt of pro-oxidant with 30%wt of CaCO₃ further reduced the elongation at break to 41% [60] after 8 days at 80 °C. The induction time has been demonstrated to be controlled by the addition of stabilisers (more specifically Irganox 1010) in the same study.

After fragmentation, biodegradation is said to proceed and a greater extent of mineralisation is attained with the addition of cellulose fibres. Biodegradation
was proven to occur from tests conducted in an industrial composting facility in Bellach near Solothurn, Switzerland in a total test period of 16 weeks. The plant has the capacity to compost about 8000 of municipal green waste per year. Composting is done in open-air windrows of 3.2 m wide, 1 to 1.2 m high and 60 m in length. The windrows are normally turned 3 time per week up to a period of 6 to 8 weeks, then turnings of 1 to 3 times per week. In the first 4 to 6 weeks, the centre of the windrows reaches temperature between 65 to 75 °C. After 12 to 18 weeks, the temperature decreases to about 40 °C due to the heat phase producing pathogen free compost.

PE carrier bags containing two AddiFlex grade, one inclusive of wood fibres were tested in by burial in the first 3m of the windrow. The samples were initially about 0.23% of the total dry weight of the green waste material. After 2 weeks, the samples entered the embrittlement stage. It was observed that the sample with wood fibres appeared to be more brittle than that without. Significant fragmentation of carrier bags was observed after 6 weeks and the integrity was completely lost at this time. Film residues of only 19.3% were detected in the first 6 m of the windrow after 12 weeks for both samples.

Photo-sensitisers are used in the Scott-Gilead technology in mulch films under the tradename of Plastor or Plastigone. The Scott-Gilead technology differs from other metal pro-oxidants by its initial function as an anti-oxidant during processing and storage. Upon exposure to UV light, the metal pro-oxidant then behaves as a pro-oxidant. This is attained through the use of dithiocarbamate as ligands of transition metals such as iron, manganese or cerium.
The mechanism by which it behaves as an antioxidant and a pro-oxidant is illustrated in Figure 29.

Initially, the complex is stable during manufacturing processing and reacts with hydroperoxides formed from thermal degradation of the polyolefin to inhibit further decomposition. However, when exposed to UV light the metal complex splits with the release of the metal in a photoactivated state which causes the rapid degradation of the polymer.

The US patent 4939194 by Scott et al[62] describes the use of photo-active dithiocarbamates of iron, manganese and cerium as pro-oxidants but dithiocarbamates of nickel, zinc, copper and cobalt as antioxidants specifically for mulch films. The application is specific as the degradation components are only UV active (not thermal) so it is only suited to applications with high UV exposure. The combination of pro-oxidants and antioxidants allow for control of the induction period of the degradable polyolefin.[63] Iron dithiomethylcarbamate (FeDMC) is the pro-oxidant and nickel dithioethylcarbamate (NiDEC) functions as the antioxidant. A significantly longer induction period is attained in the presence of NiDEC and with lower concentrations of FeDMC.

The control of highly active photo and thermal pro-oxidants such as β-diketones could also be approached with the dithiocarbamate antioxidants. β-diketones such as iron acetylacetonate (FeAcAc) alone is generally unsuitable as a pro-oxidant due to its high degradation rate of the polyolefin during processing. However, when used in combination with Zn, Co, Cu or Ni dithiocarbamate, excellent thermal stability during processing is obtained and
a short induction period is attained in the degradable polyolefin followed by a rapid rate of degradation.[62] To further expand the suitability of dithiocarbamates to other applications such as packaging, Scott later produced a patent to employ metal carboxylates (and/or β-diketones) as pro-oxidants and the dithiocarbamate antioxidants for such purposes. US patent 2006/0160922[64] disclosed the use of transition metal stearates (such as iron, manganese and cobalt) in combination with dithiocarbamates of zinc, calcium and manganese. Cobalt stearate has been preferred over other transition metals as it was found experimentally that cobalt gave the best balance of pro-oxidant and antioxidant properties. Zinc di-iso-nonyl dithiocarbamate (ZnDNC) has been the preferred antioxidant. The induction period and lifetimes is adjusted by altering the concentrations of cobalt stearate and ZnDNC. More specifically, the preferred antioxidants ranges are between 0.01 to 0.5%wt of the final product and the preferred pro-oxidant ranges are between 0.05 to 4 %wt of the final product.

No biodegradation studies confirm that the Scott-Gilead technology will be compostable or mineralise further by micro-organisms. It is expected that after fragmentation of the polyolefin to molecular weights below 10,000, it is possible that mineralisation may occur. However, it is worthy to note that dithiocarbamate pro-oxidants are only photo-sensitive and not thermally sensitive.
4.2. Carbonyl Containing Copolymers

4.2.1 Carbon-monoxide copolymers

Ethylene and carbon monoxide has successfully incorporated photo-sensitive carbonyl moieties into the polymer backbone to yield carbon-monoxide copolymers[65] (Figure 30). The carbonyl group can absorb UV light in a broad absorption band extending beyond 340 nm[66] and undergo primarily Norrish II reactions (little Norrish I) to cause chain scission of the polymer chains to shorter segments. Some of the commercially available products are from Dow Chemical, Du Pont and Union Carbide for six-pack carrier rings for beverage containers.

The current poly(ethylene-co-carbon monoxide) copolymers (ECO copolymers) have been limited to low density polyethylene (LDPE) due to limitations imposed by the catalytic system employed during polymerisation. Furthermore, the level of CO groups incorporated into the polymer chains have also been limited to below 2%[65]. The degradation rate is dictated by the number of carbonyl groups present as chain scission will only occur at the carbonyl group locations along the polymer chain. Hence blending of a concentrated ECO copolymer with a homopolymer will not yield the same degradation rate as the pure CO copolymer with the same amount of carbonyl groups[65]. In addition, an increase of CO groups in the backbone is accompanied by absorption of light in the longer wavelengths which will degrade in normal room illumination, decreasing its shelf-life[67].

It is expected that upon fragmentation of the polymer film, it is accompanied by a molecular weight reduction and enhanced hydrophilicity which allows
bioassimilation by micro-organisms to occur slowly. However, such biodegradation process has not been confirmed in scientific documents or confirmed beyond doubt[68]. Photodegradation of ECO copolymers were studied in air and in marine environments[69] as their primary uses are for six pack beverage carrier rings, which can end up in marine environments as litter. The ECO copolymer contained 1%wt of CO, which exhibits absorption maxima at 279 nm. The short wavelength coincides with the “tail” of the solar spectrum thus the copolymer is stable behind glass or under diffused light. When samples were exposed to air on the roof of a building, the sample showed rapid degradation within 6 weeks, losing nearly 99% of the initial elongation. The sample had exhibited a high degree of embrittlement at this stage and crumbled upon handling. When samples were exposed to a marine environment by placing the samples in a tank of sea water, rapid degradation had also occurred within 6 weeks, similarly to that in air. This was indicated by the loss of ~ 95% of the initial elongation value. However, the degree of embrittlement was much less than that in air until after 14 weeks of exposure.

4.2.2 Vinyl ketone copolymers

Guillet et al released a patent (US 3,753,952) in 1973 on polymerisation of a vinylidene monomer (such as ethylene, methyl methacrylate and styrene) to contain a ketone carbonyl group at a carbon immediately adjacent to the backbone chain of the polymer[67] (Figure 31). This is the distinguishing difference to carbon monoxide copolymers where the carbonyl group has been incorporated into the main polymer chain (Figure 30). Through the
different location of the carbonyl group, the efficiency of the chain scission process becomes higher than carbon-monoxide copolymers.

The vinyl ketone copolymers has been commercialised under the tradename of Ecolyte[65] which is sold as a masterbatch. The uses of Ecolyte include mulch films as well as packaging.

The amount of ketone carbonyl groups dictates the rate of degradation, which is limited to 0.02 %wt to 2 %wt[67]. However, CO levels above 1%wt tend to decrease the polyethylene properties. Other factors affecting the rate of degradation are the substituents R$_1$ and/or R$_2$, blending with resins in different ratios from 1:20 to 1:9[65] and the final thickness of the article. The carbonyl group absorb light with maxima between 280 to 330 nm depending on the substituents and undergo Norrish I and Norrish II photochemical reactions to cause chain scission. In the case of ethylene-co-methylvinyl ketone and ethylene-co-methyl isopropyl-ketone copolymers, Norrish II reaction dominates to direct cleavage of the polymer backbone. Norrish I reaction is important in the formation of tertiary radicals initiating chain hydroperoxidation to cause rapid embrittlement.

Similarly to carbon-monoxide copolymers, photodegradation initiate chain scission of the polymer into fragments of lower molecular weight. Bioassimilation is expected to proceed by digestion from micro-organisms. However, no scientific documentation is evidenced to confirm such process taking place[68].
4.3 Other Novel Commercial Products

4.3.1 Chemo-taxis approach

Another commercial prodegradant for polyolefins is manufactured by Bio-Tech Environmental that utilises organic bioactive additives to induce break down of the polymer. It takes an alternative approach to oxidative degradation by attracting micro-organisms (described as chemo-taxis in their patent) by effectively providing food in the additive hence micro-organisms can colonise and digest the polymer. To initiate break down of the polymer, the additive includes a swelling agent, which expands the polymer molecular structure to allow sufficient space for micro-organisms to colonise.

The first generation product called “Bio-batch” is sold as a masterbatch and can be directly compounded into other polymers during processing at a level between 1 to 5%wt. US patent 2008/0103232 disclosed the use of “chemo attractants” based on furanone in combination with swelling agents such as natural fibres or cultured colloids. Other essential components include glutaric acid, hexadecanoic acid compound, polycaprolactone in a carrier resin (EVA)[70]. Some suitable furanone compounds are 3,5-dimethyl-pentenyl-dihydro-2(3H)-furanone isomer mixtures, emoxyfurane and N-acylhomoserine lactones (Figure 32). It should be noted that the furanone structure contains the UV active carbonyl structures. Halogenated furanones are excluded as suitable “chemo attractants” as they are quorum sensing inhibitors which causes significant reduction in quorum sensing microbes.

A wide range of bacteria listed in the patent is attracted to such furanone compounds. Other “chemo attractants” listed includes sugars that are not
metabolized by the bacteria such as glucose, succinate, etc but most preferred is non-esterified starch.

5. **Controlling the Degradation rate**

The required service life of an oxo-biodegradable polyolefin is dependant on its end use. This can typically vary from a few weeks to a year or more. For example, it would be desirable for a drink bottle to degrade quite soon after it has been disposed of whereas a mulch film would require a much longer life time. There are numerous methods that may be used to control the rate of degradation and these are discussed below.

5.1 **Choice of metal**

The photocatalytic activity of a series of different transition metals in polyolefins has been reported.[4] Figure 33 shows the effect of different metal 2, 4-pentanedione complexes on UV ageing of LDPE film. The carbonyl index as a measure of degradation is explained in more detail in later sections of this report. With the exception of the titanyl complex, all additives showed an incubation period before oxidation commenced with the observed photodegradation efficiency of the metals decreasing in the following order:

\[
\text{Ti} > \text{Al} > \text{Zr} > \text{VO} > > \text{Cu}
\]

From the results in Figure 33 it can be observed that copper exhibits some photo stabilizing activity.
The effects of metal 2, 4-pentanediol complexs were also reported in PP film. The ferric complex showed the highest photoactivity of all metal complexes studied. The photodegradation efficiency decreased in the following order:

\[
\text{Fe} > \text{Ti} > \text{Zr} > \text{Mg} > \text{V} > \text{Cu} > \text{Ca} > \text{Al}.
\]

The vanadyl and copper complexes showed distinct induction times followed by rapid degradation. Calcium and magnesium were also included in the series and the photoactivity from these is suspected to be from the carbonyl functionality of the organic moiety rather than the metal itself. Interestingly, the aluminium complex showed greater activity in PP than in PE.[4]

Synergistic mixtures of metal ions have also been reported in accelerating degradation. An example is the use of a mixture of 0.005 % zinc dibutylthiocarbamate and 0.005 % iron dibutylthiocarbamate. This provides a faster rate of degradation compared to 0.01 % of either additive alone.[9]

### 5.2 Prodegradant : Antioxidant ratio

Antioxidants and other stabilizers are commonly used in commercial polyolefins. As discussed earlier in this report, the mechanism of oxidative degradation involves initiators such as hydroperoxides which lead to the formation of free radicals. From this it follows that antioxidants and stabilizers can fall into two categories:[1]

1. *chain breaking antioxidants* (to deactivate alkylperoxyl radicals) and
2. *preventative antioxidants* (to destroy or neutralize hydroperoxides)
Chain breaking antioxidants include phenols or arylamines where the chain reaction can be stopped via delocalisation of charge in the aromatic ring and/or by steric hindrance or via hydrogen abstraction in arylamines. Examples of chain breaking antioxidants include 2, 6-di-tert-butyl phenols (e.g. BHT), vitamin E (α-tocopherol), lignin and tannin. Other examples include the hindered aminoxyls (>N-O') which are “stable” radicals that can remove a hydrogen to form a stable molecule. These are well known commercially as HALS (Hindered amine light stabilisers).

Preventative antioxidants can be classed into three major categories:[1]

a) peroxide decomposing
b) metal deactivation (generally involving metal ion chelation)
c) UV absorbing additives

In order to control the onset of prodegradant activity and consequently, the lifetime of the polymer, antioxidants are often employed. The successful use of such systems has been previously reported in mulch films.[71] For example, light stable transition metal dithiocarbamates \([R_2NCSS]_2M\) can exhibit both peroxide decomposing and metal deactivating antioxidant behaviour. Iron salts act as stabilizers initially but then are photochemically converted to prodegradants. As discussed in the previous section on commercially available prodegradants, this technology is often better known as Scott-Gilead technology and is used in Plastigone and Plastor tradename products.
WO2006/043827 patent (assigned to NOR-X) describes the combined use of a prodegradant and stabilizer to adjust the lifetime of thermoplastic polymers.[56] The stabilizers described here are similar to those described in the above categories and include phenolic antioxidants, radical scavengers (chain breaking antioxidants), organic phosphites (peroxide decomposing additives) and UV absorbers. The common feature is that the stabilizer decreases the concentration of reactive free radicals.

The NOR-X patent also describes some differences between process stabilizers (to ensure the polymer does not degrade at the processing temperatures e.g. hindered phenols, organic phosphites) and long term stabilizers (ensuring stability during storage or use, e.g. UV absorbers and hindered phenols). It is also essential that the prodegradant does not overrule the effect of the process stabilizer before processing is complete. The patent discloses that a controllable lifetime of polymer from 3 days to 5 years is possible with the choice of prodegradant and stabilizer.

It is also interesting to note that the oxidising ability of a prodegradant can be enhanced if it is prepared with the use of an oxidizing agent such as hydrogen peroxide. The NOR-X patent WO2006/043827[56] gives examples of such prodegradants based on iron stearate. It also describes methods whereby oxidizing ability of a prodegradant additive can be measured against iodide or phosphite as reducing agent.

5.3 Effect of pigments and dyes

The patent US 4360606 mentions organic dyes being employed as photosensitizers.[44] Examples given include Acridine Orange and Yellow,
Alizarin, Azure B, Brilliant Green, Bromothymol Blue, Congo Red, Crystal Violet, N, N-Dimethyl-p-phenylazoaniline and Methylene blue. The chemical structures of some of these dyes reveal some similarities to some of the structures listed as prodegradants, for example, Alizarin is based on an anthraquinone type structure. Most other dyes contain highly conjugated unsaturated ethylene double bond groups.

In addition to organic dyes, inorganic pigments such as TiO$_2$ and ZnO that are often added to whiten the polymer can also influence the degradation rate. As mentioned in the earlier section of this report, the photoactivity of these additives is dependant on particle size, surface treatment and crystalline form as well as any metal ion dopants that may be used.

5.4 Other

The combination of metallic and non-metallic photoinitiators has been investigated with a mixture of cobalt stearate and benzil (an aromatic diketone).[72] LDPE films containing varying amounts of cobalt stearate and benzil were prepared. Cobalt stearate was highly effective in accelerating the photodegradation of LDPE films at low concentrations. The addition of benzil to cobalt stearate decreased the rate of degradation compared to cobalt stearate alone and a retarding effect was observed when benzil alone was added to LDPE. This result is surprising, since benzil is commonly used as a photoinitiator and could be expected to accelerate the degradation rate. The paper describes the retarding effect of benzil on the basis of radical recombination.
6. Polyolefin Biodegradation

Polyolefins are high-molecular weight polymers, hydrophobic and thus not easily degraded by abiotic or biotic factors.[73-75]. Due to their massive size, these molecules are unable to enter microbial cells to be digested by intracellular enzymes and they are inaccessible to the action of extracellular enzymes produced by microorganisms due to their excellent barrier properties. Exposure to UV and heat is known to promote degradation of most polymers but polyolefins degrade very slowly under environmental conditions.

It has been reported that UV-irradiation of PE for 16 days before incubation into soil evolved <0.5% carbon by weight after 10 yrs as compared to an non-irradiated polyethylene sheet that produced <0.2% CO₂.[76] Another study found that polyethylene did not degrade in moist soil even after incubation for almost 12 yrs[74] and only partial degraded after being buried in soil for 32 yrs.[77] Further it was suggested that at such slow rate, it would take approximately 300 yrs to entirely degrade 60 μm LDPE films in soil.

The mechanism of abiotic photo-oxidation of PE resulting into formation of carbonyl compounds is presented in Figure 1, section 2.1. Photo-or thermal-oxidation of high-molecular weight polyolefins into low-molecular weight products is vital because so far only oxidized polyethylene products (500 – 5000 Da maximum) are known to be degraded and assimilated by microorganisms.[6, 53, 78-80]

A growing number of patents (as discussed in Section 4) are secured by scientists working in the field of degradable polyolefins. A number of companies have also launched their products into the market namely Addiflex, Ciba Envirocare™ and AGP™, ECM Masterbatch Pellets by ECM Biofilms,
EcoSafe Biodegradable Compost and TDPA®. Most of these products are claimed to be biodegradable and frequently used in research studies. However, caution is advised since fate of their degradation products in the environment is not clearly known.

6.1 Microbial Biodegradation

There has been extensive research into biodegradability of polyolefins containing pro-oxidants in the presence of microbial consortium present in the environment as well as selected microbial species in defined medium under controlled laboratory conditions. It is now widely accepted that abiotic oxidative degradation of high molecular weight polyolefin into low molecular weight compounds is necessary to facilitate action of microorganisms and/or enzymes. In most studies, the methods of assessment of polymer biodegradability include gravimetric or molecular weight loss, carbonyl index, tensile strength and elongation, SEM analysis of film surface etc. It has also been suggested that microorganisms capable of adhering to the polymer surface and growing there, produce biosurfactants important for adhesion and possibly degrade oxidation products and poorly soluble substances.[81, 82] Koutny et al.[83] reported that beta and gamma-Proteobacteria and high G+C Gram +ve Rhodococcus strains formed biofilms on the surface of oxidized low-density polyethylene film containing prooxidant additives, thus suggesting their role in assimilation of oxidized polyethylene film. Albertsson et al.[84] studied thermo-oxidative degradation of polyethylene for 3.5 yrs and reported that organic acids (extractable compounds up to 12-carbon lengths) produced during degradation process were not detected in the end as they were
probably utilized by *Arthrobacter paraffineus*. Similar results were reported by Roy et al.[85] who has reported that degradation of low-density polyethylene films (containing cobalt stearate as pro-oxidant) by enriched microbial species belonging to genus *Bacillus* resulted into utilization of extractable oxygenated and non-oxygenated low mol wt compounds, approximately 8% weight loss of the polymer and an increase in the bacterial count. Yamada-Onodera et al.[79] studied biodegradation of PE incubated with *Penicillium simplicissimum* and suggested that microorganisms might even have a role to play during degradation of high-mol wt polyethylene. Few other studies have also reported colonization of oxidized polyethylene film surface by fungi.[54]

Addition of surfactants such as Tween 80[86] and other additives such as Mn(II)[87], mineral oil[88], ethanol[89] in the test medium has been reported to enhance biodegradation of polyethylene by microorganisms. Albertsson et al.[86, 90] reported that addition of surfactant Tween 80 to the liquid culture medium of *Pseudomonas aeruginosa* containing polyethylene film enhanced biofilms formation possibly due to increased hydrophilicity of PE surface. It is considered important to select a detergent which has chemical properties compatible with biosurfactants to facilitate microbial adhesion on the polymer surface. Non-ionic surfactants such as Tween-80 adsorb on the surfaces with either hydrophilic or hydrophobic groups oriented towards the surface, depending on the nature of the surface. In polyethylene, since there are no polar groups available, the surfactants will probably be oriented with the hydrophobic group towards the surface making it more hydrophilic. Ionic surfactants (particularly anionic ones) in an aqueous medium leads to denaturation of proteins with massive binding of the surfactant to the proteins.
In contrast non-ionic surfactants, such as Tween-80, are not capable of denaturing proteins/enzymes and their main action is to detoxify some unsaturated fatty acids which would otherwise prohibit microbial growth on the PE surface.[86]

This view was later shared by another researcher[88] who suggested that surface characteristics of microbial cells can play crucial role in cell adsorption and utilization of insoluble products. This study reported that bacteria *Rhodococcus rubber* degraded approximately 8% of polyethylene films in 30 days, and addition of mineral oil enhanced colonization of PE surface and its subsequent degradation by almost 50% (Figure 34).

Recent studies have reported PE degradation by selectively cultured members of *Actinobacteria*, comprising of various strains of *Rhodococcus*[88, 91, 92] (Figure 35) and *Pseudomonas*[93].

Orhan and Buyukgungor[94] studied biodegradability of polyethylene films in soil inoculated with cultures of *Phanerochaete chrysosporium* and found that degradability of polyethylene films enhanced as compared to films incubated in soil with no microbial enrichment. Another study has reported almost 11% (gravimetric) and 30% (molecular) weight loss of PE in liquid medium inoculated with thermophillic strain of genus *Brevibacillus*[95] However, such experiments do not simulate real-time exposure conditions where a complex microbial community is present and variable abiotic and biotic factors influence the biodegradability of polyethylene.

Blending of polyethylene with degradable materials such as starch tends to enhance the biodegradability of PE. Starch is a hydrophilic material and it
degrades easily by when exposed to moisture or biotic environment. Hydrolysis of starch makes the PE structure porous, increasing the polymer surface accessible for the attack both of biotic and abiotic factors and thereby accelerating degradation process.[54, 96, 97] Lee et al[98] was first to report degradation of PE containing pro-oxidant and 6% starch by three lignin-degrading Streptomyces sp. Later, Albertsson et al[84] studied degradation of LDPE films containing starch filler and a pro-oxidant (styrene-butadiene copolymer and manganese stearate) in an aqueous media inoculated with alkanes and alkenes degrading species - Arthrobacter paraffineus and Verticillium species and found that A. paraffineus inoculated samples had higher starch-removal capability as compared to samples inoculated with fungal strains (Figure 36).

Further, it has been reported that the biodegradability of LDPE/starch blends is significantly enhanced if the samples are exposed to UV radiations prior to soil burial. A study found 20-66% reduction in tensile strength of UV oxidized starch-blend polyethylene samples exposed to soil burial test as compared to 10-26% reduction in tensile strength for samples inoculated in soil without UV irradiations.[99]

In addition, Fourier transform infrared spectroscopy (FTIR) spectra was acquired for the samples and carbonyl index (CI)[100] measured for LDPE/starch blends exposed to UV and UV/soil burial treatment was higher than pure LDPE samples treated in the same manner. These results suggested that UV exposure of LDPE/starch blends, prior to soil burial significantly enhances its biodegradability - (Figure 37).
An overview of studies which suggested biodegradation of polyolefins (with/without pro-oxidants and fillers) in the presence of different microorganisms is presented in Table 3.

6.2 Enzymatic Biodegradation

Enzymes are biological macromolecules that catalyse chemical reactions. Like all catalysts, enzymes bind to the substrates, lowering the activation energy thus inducing an increase in reaction rates in an environment otherwise unfavourable for chemical reactions. Majority of enzymes are proteins having a polypeptide chain with a complex three-dimensional structure, which folds and pockets create active site, where the interaction between the enzyme and substrate takes place leading to a chemical reaction, resulting into particular product. Enzymes are very selective for their substrates and they are known to catalyze a large number (approximately 4000) biochemical reactions. Some enzymes do not need any additional component for their optimal activity and others require non-protein molecules called cofactors, to be bound for activity. Inorganic cofactors include metal ions such as sodium, potassium, magnesium or calcium and organic cofactors, also known as coenzymes include different B-vitamins (thiamine, biotin etc) and metabolic compounds (NAD+, NADP+, FAD+ and ATP+ etc). Enzymes are named and numbered according to rules adopted by the International Union of Pure and Applied Chemistry (IUPAC). The main classes of enzymes are: (1) Oxidoreductases - catalyse oxidation/reduction reactions; (2) Transferases - transfers a functional group; (3) Hydrolases - catalyse the hydrolysis of various bonds; (4) Lyases - cleaves various bonds by methods
other than hydrolysis and oxidation; (5) Isomerases - catalyse isomerisation changes within a single molecule; (6) ligases - join two molecules with covalent bonds.

High molecular weight polymers are not easily susceptible to enzymatic biodegradation as they are unable to enter microbial cells due to their large size. To accomplish scission, microorganisms secrete specific enzymes or generate free radicals, which act on polymer chains and break them down into oligomers, dimers and/or monomers. Chandra and Rustgi presented a brief description of enzyme mechanisms, biological oxidation and biological hydrolysis (Figure 38). During biological oxidation reactions, hydroxylases (also called mono-oxygenases) catalyse insertion of a single atom of oxygen in the substrate A as part of hydroxyl group (Figure 38, equation 1) and require a second reduced substrate BH2 which simultaneously undergoes oxidation (i.e. dehydrogenation). Usually this second substrate is NADH. On the other hand, oxygenases (also known as di-oxygenases) catalyse insertion of two oxygen atoms or an oxygen molecule into substrate, forming peroxyl groups (Figure 38, equation 2) that are more easily fragmentable. In cases where oxygen molecule acts as a hydrogen/electron acceptor, enzymes catalysing the reactions are called oxidases, and H2O (Figure 38, equation 3) or H2O2 (Figure 38, equation 4) are produced. Most lignolytic microorganisms produce oxidases. During biological hydrolysis, proteolytic enzymes catalyse the hydrolysis of peptide bonds (Figure 38, equation 5) and ester bonds (Figure 38, equation 6).
Biodegradable polymers and some of the recalcitrant polymers such as polyolefins are subject to biodegradation, and microbial enzymes are considered to play key role during the process.[101-104] Biofilm formation on the surface of polyethylene substrates and utilization of low molecular weight degradation products by microorganisms has been reported by a number of studies[53, 54, 91-93, 105-107] but there is limited information on relevant enzymes involved in the process. Pometto et al[108] reported that lignocellulose-degrading Streptomyces species produce extracellular polyethylene-degrading enzymes, however there has been no clarity regarding their structure and/or activity i.e. rate and types of reactions catalysed during PE-biodegradation. Few years later, Iiyoshi et al[87] reported studies on degradation of high-molecular weight polyethylene membranes by lignin-degrading fungi ZU-154 and Phanerochaete chrysosporium. Both the fungi were found to produce manganese peroxidase (MnP) and the enzyme production was accelerated on addition of Mn(II) to the culture medium suggesting that manganese could acts a cofactor for MnP enzyme during degradation of polyethylene. Further research into exact role of reported enzymes[87, 108] is needed to have better understanding of mechanism of polyethylene degradation.

6.3 Mechanism of Biodegradation

There is an on-going debate regarding biodegradability of polyethylene and this has been mainly attributed to our present understanding on role of microorganisms,[53, 79, 80, 95] and limited information available on enzymatic biodegradation.[87, 108] As a result it is difficult to have any clarity
on mechanism involved in polyolefin degradation. Our present understanding of PE biodegradation mechanism is based on Albertsson et al.[100] study, which proposed that since linear polyethylene structure is similar to linear paraffin molecules, it is likely that they have similar biodegradation mechanisms. During biodegradation process, microorganisms or enzymes produced by the microorganisms act on abiotically oxidized polyethylene degradation products and eventually form fatty acids (Figure 39), which is then transported inside the cell where it undergo β-oxidation and completely mineralize into carbon dioxide, water and biomass.[100] However, it is still not clear if low-density PE products are assimilated as such by microorganisms or further degraded into smaller molecules by abiotic or biotic processes before being transported inside the cell.[91]

There have been few studies that proposed that lignolytic enzymes produced by lignin-degrading microorganisms could play a role in polyethylene degradation.[98, 108] However, the basis of such propositions is debatable as there is no similarity between chemical structures of polyethylene and lignin. Polyethylene consists of long chains of monomer ethylene \((C_2H_2)_n\), whereas lignin has a complex racemic macromolecular structure, formed by crosslinking of three methoxylated monolignol monomers (Figure 40).

Cell membrane plays important role in the interaction of microorganisms with different substrates. It acts as a permeability barrier and provides a site for transfer of molecules inside or outside the cell. An interaction between PE film surface and cell surface is important. Based on the information available from the published studies, Koutny[91] has proposed different possibilities which
are available for biodegradation of abiotically oxidized polyethylene films (Figure 41).

The colonization of polyethylene surface by microorganisms and their utilization of low-molecular weight polyethylene products, starch or other additives ‘suggests’ that they are involved in polyethylene biodegradation but further research into understanding the actual mechanism involved is needed. To the best of our knowledge, there is no published study that has reported isolation of efficient polyolefin-degrading microorganisms and/or demonstrated biodegradation process in the presence of pure culture. This needs to be rephrased correctly as there are some reported studies that used pure cultures during PE biodegradation study and loss of weight, SEM of bugs growing on films and chemical composition of the medium were considered as indirect proof of (slow rate) PE biodegradation but none of the studies confirmed that PE was completely assimilated in the presence of these bugs.

Traditional cultivation methodologies are generally used for isolating microorganisms from environmental samples however, this approach is biased and majority of bacterial diversity has never been cultured using these classical methods. It is likely that microorganisms actively involved in degradation of oxidized polyethylene products although present in nature, have not yet been identified and isolated. Using cutting edge molecular ecological techniques, it is possible to identify efficient polyethylene-degrading microorganisms, although specialized techniques would be required to culture them under laboratory conditions. It is also suggested that polyolefins being complex molecules, their degradation would be the result of a microbial synergy. Koutny[91] proposed that complex microbial communities present in
soil or compost are more likely to degrade oxidized polyethylene films than pure cultures as there is much wider range of enzymes/other essential metabolites available that would assist the process of degradation as compared to few enriched cultures. However, polyolefin degradation in environmental samples is extremely hard to interpret and detection and/or isolation of relevant polyethylene degrading microorganisms will greatly simplify such studies, and provide better understanding of the mechanisms involved.

7 Standard Accelerated Ageing Test Methods

Degradation of polyolefins is induced by different factors and mechanisms and depending on the nature of causing agents that trigger degradation (i.e. UV, visible light, moisture, heat, microorganisms etc), the process is classified as photo-oxidative degradation, thermal degradation, biodegradation, hydro-biodegradation and oxo-biodegradation. Degradation of polyolefins that occur by any one of these mechanisms can be assessed by measuring changes in physical appearance, molecular weight, amount of carbon-dioxide evolved and by enumeration of microbial growth on polymer surface after exposure to natural environments such as soil, compost, fresh water/marine water and sewage-sludge. Standard test methodologies and accelerated ageing practices have been developed and published by international Standards authorities namely American Society for testing and Materials International (ASTM) www.astm.org; Standards Australia (AS) www.standards.org.au; British Standards (BS) www.bsi-global.com; European Committee for Standardization (CEN) www.cenorm.be; German Institute for Standardization...
7.1 Photodegradation

Photodegradation involves degradation of materials upon exposure to UV or visible light. Photodegradation of polyolefins is assessed either using natural sunlight (outdoor exposure methods) or by using weatherometers (indoor exposure method). Outdoor exposure tests require much longer exposure periods (up to few years) for completion as compared to laboratory based test methods. For outdoor exposure, ASTM 5272-08 and ISO 877:1994 standard test methods are available that provide guidelines to evaluate photodegradation of polymers at a specific site in terms of predicting expected life of the polymers. However, it has to be taken into account that due to variability in test conditions (temperature, moisture, UV intensity & duration and other climatic conditions) it is not possible to make a comparison between data obtained from degradation of same polymeric material at two different geographical sites.

ASTM D5272-08 is used for the outdoor exposure testing of photodegradable plastics. According to this test, specimens are mounted on exposure racks, which are positioned in a way that the specimens face the equator and so that
the exposed surfaces are at 5 ° angle from the horizontal. The UV radiometer is mounted at an angle similar to that of the specimens (i.e. at 5° angle). The test is run for desired amount of time (12-18 months) to ensure that samples are exposed to maximum and minimum intensities of UV light (295 to 385 nm) during the test period. At the end of the test, samples are analysed for loss in physical and chemical properties such as gravimetric and molecular weight, tensile strength and elongation (in accordance with test methods included in the Standard ASTM D5272-08). The Standard provides provision for testing degree of oxidation of polyolefins using carbonyl index, which is a ratio of carbonyl infrared absorbance at approximately 1715 cm⁻¹ to an invariant absorbance characteristic of the polymer (for example, C-H stretch is approximately 3000-2840 cm⁻¹). The degradation end point of polyolefins can be determined by a tensile test.

For in-lab testing, laboratory weatherometers allow accelerated UV degradation of materials under controlled environment. Xenon-arc and UV-fluorescent are main types of weatherometers. Xenon-arc weatherometer comprises of a long arc, water-cooled xenon lamp equipped with borosilicate inner and outer filters as the light source and the irradiance spectrum closely resembles natural daylight.[111]

UV-fluorescent weatherometers consist of fluorescent UV lamps and unlike xenon-arc, only emits light spectrum in the UV region (<400 nm). There are different UV lamps for different UV light ranges, for example the UVA-340 lamps would emit light from 300-400 nm. A solar eye system can be fitted into weatherometer, which automatically adjusts the intensity of each lamp to provide a constant irradiance throughout the exposure duration.
ISO 4892-2:2006 is one of the most commonly used standard and it specifies the methods for exposing specimens to xenon-arc light in the presence of controlled conditions (temperature, humidity and/or wetting) to reproduce the weathering effects that occur when materials are exposed in actual end-use environments to daylight or to daylight filtered through window glass.

There are several standard test methods, which are currently available to assess stability of polymers in the presence of air and light source and they are listed in Table 4. Test samples are incubated according to the guidelines provided in respective standards.

7.2 Thermal degradation

The rate of thermal oxidation is slow at ambient temperatures therefore, as reported in literature, thermo-oxidative tests are carried out by placing extruded films in air-oven, at high temperature for extended periods. Tensile properties, carbonyl index, melt flow index and density are mainly used for assessing level of degradation.[3, 53, 112-114] Jakubowicz[112] studied thermal-oxidation of polyethylene and reported that the average molecular weight of polyethylene was estimated as 5000 Da after 2 weeks at 70 °C and after 8 weeks at 60 °C, suggesting that temperature was an important factor that influenced rate of degradation process. He further observed that oxygen concentrations in the range of 5-20% did not have any effect on rate of degradation at these two different temperatures. There are several standard test methodologies available, which provide guidelines to assess thermal degradation of polymers under controlled conditions (Table 5).
Standard ASTM D5510 – 94 is intended for use in evaluating plastics, which are designed to oxidized easily, after use. The practice defines the exposure conditions of plastics at various temperatures, when exposed solely to hot air for extended periods of time. The method recommends that practise D3826 be used to determine the embrittlement endpoint, which is defined as that point in the history of a material when 75% of the specimens tested have a tensile elongation at break of 5% or less at an initial strain rate of 0.1 mm/mm min. There are two types of ovens included in this practice; Gravity-Convection oven (film specimens thickness <0.25 mm) and Forced-ventilation oven (film specimens thickness >0.25 mm), and procedure used for each oven-type is different. According to the standard, test specimens are mounted on frames and placed in oven such that both sides of the specimens are exposed to air flow (may even be repositioned periodically). When tests at a single temperature are used, all materials must be exposed at the same time in the same device so that results of tests can be compared by analysis of variance or a similar statistical data analysis procedure. When testing at series of temperatures are used, exposure temperatures are selected such that the lowest temperature should produce the desired level of property change or product failure in approximately six months and next higher temperature should produce the same level of property change or product failure at approximately one month. The third and fourth temperatures should produce the desired level of property change or product failure in approximately 1 week and 1 day respectively. A table of suggested temperatures and exposure times is included in the standard.
7.3 Biodegradation

Biodegradation is a process of degradation, which is initiated or propagated by microorganisms such as bacteria and fungi. For a polymer to be labelled biodegradable, it is important that polymer fractions are assimilated by microorganisms and completely mineralised into carbon dioxide, water and biomass, without leaving any toxic residue. Biodegradation testing follows inoculation of test materials in environmental samples such as soil, compost, sewage, fresh or marine water under simulated or real-time exposure conditions. There are several standard test methods and drafts available (Table 6), which are frequently used to assess biodegradability of polymers by measuring molecular weight and molecular weight distribution, tensile properties, weight loss, extent of fragmentation, enzyme assays, biochemical oxygen demand, carbon dioxide production and ecotoxicity. A combination of test procedures is used during evaluation to confirm that biodegradation has actually occurred. For example, weight loss may result from leaching of additives or dispersion of low-density products into surrounding environment, carbon dioxide production in starch blend polymers might result from degradation of starch and other low molecular weight fractions, with no degradation of large molecular weight polymer chain.[68] It is recommended that selection of test methodology be based on potential fields of application of the test polymer and its fate at the end i.e. compost, soil, fresh or marine water. Some of the widely used standards are: AS4736; ASTM D5338; ASTM D6002; EN 13432; ISO 14855 (for compost exposure), ASTM D5988; ISO 17556 (for soil exposure) and ASTM D6691; ASTM D6692; ISO 15314; ISO 16221 (for marine exposure) (Table 6).
The strictest European standard for biodegradability is EN 13432. This standard is a reference point for all European producers, authorities, facility managers and consumers. The standard specifies requirements and procedures to determine the compostability of plastic packaging materials based on four main areas, biodegradability; disintegration during biological treatment; effect on the biological treatment process; and effect on the quality of the resulting compost. This standard can apply to other packaging materials in addition to polymers, and incorporates following tests and standards, ISO 14855; ISO 14852; ASTM D5338-92; ASTM D5511-94; ASTM D5152-92; ASTM E1440-91; modified OECD 207; and CEN TC 261/SC4/WG2.

Biodegradability of polyolefins has been studied for many years and it has been reported that oxidized low-density polyethylene is degraded and assimilated by microorganisms. Most studies have used either respirometric method (evolution of carbon dioxide) or microbial consortium for evaluating biodegradability. Jakubowicz[112] studied thermo-oxidative degradation of polyethylene films using accelerated test conditions and their subsequent mineralization using soil burial test. The study has reported that after 180 days of incubation in soil, microorganisms assimilated almost 60% of abiotically oxidized polyethylene fragments. Few recent studies have proposed new insights into data interpretation to evaluate polymer biodegradability. Biodegradation of oxidized polyethylene films was studied in soil and compost[3, 53] and it was observed that once the oxidation reached a plateau, molecular weights drop significantly (values lower than 6000 Da) along with production of low molar mass, oxidized fractions, which become accessible to action by microorganisms. Based on the results obtained in
these studies, it was proposed that the molecular weight carbonyl index relationship could be used to predict the potential assimilation by microorganisms.

Another recent study by Chiellini et al[107] assessed degradation of thermally-oxidized LDPE film in an aqueous medium (river water) by monitoring the amount of carbon dioxide produced over time in a respirometric apparatus. After 100 days, 12% and 48% mineralization was achieved for oxidized polyethylene fragments, collected from medium and high levels of oxidation, and their corresponding acetone extractable fractions containing significantly different amounts of oxygenated groups. It was observed that rate of biodegradation was significantly high from samples collected at higher oxidation values. Based on these results it was proposed that structural characterization of thermally oxidized polyethylene fragments could be used for predicting their ultimate fate in river water at the end.

Polyolefins are known to degrade by oxo-biodegradation mechanism and there is single standard method developed and published namely, ASTM D6954 – 04, *Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation*. The scope of this standard provides a framework to compare and rank controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal and photooxidation processes as well as the biodegradation and ecological impacts in defined applications and the disposal environments after degradation. The conditions selected for oxidation (UV or thermal at 20 °C to 70 °C) accelerate the degradation likely to occur in a chosen application and disposal environment. The residues resulting from
abiotic oxidation are then exposed to appropriate disposal or use environments in standard biometric test methods to measure the rate and degree of biodegradation. Finally, the end-residues must be submitted to aquatic and terrestrial toxicity tests (E 1440, OCED guideline 207 and OCED guideline 208) to ensure that they are environmentally benign and not persistent. Each degradation stage is independently evaluated to allow a combined evaluation of a polymer’s environmental performance under controlled laboratory setting. According to the standard, the results of laboratory exposure cannot be directly extrapolated to estimate absolute rate of deterioration by the environment because the acceleration factor is material dependent and can be significantly different for each material and for different formulations of the same material. However, exposure of a similar material of known outdoor performance, a control, at the same time as the test specimens allows comparison of the durability relative to that of the control under the test conditions.

8 Toxicity of degradable polyolefins

Polyolefins are basically inert and to enhance their degradability, prodegradants are added during processing. It is vital to know the effect of degradation products as well as additives on the environment to ensure that they do not contribute toward ecotoxicity. According to National Industry Chemical Notification and Assessment Scheme or the EU Directive 67/548/EEC, a polymer in order to be degradable must not contain any additive that are classified or may be classified as carcinogenic, mutagenic or tetragenic according to the approved criteria for the classification of hazardous
substances by the National Industry Chemical Notification and Assessment Scheme; must have a minimal natural material or starch content of 30%; plastic additive must not include more than 40% aromatic polyesters or other degradable plastic by weight; the germination rate and the plant biomass of the sample composts of plant species should be more than 90% of those from the corresponding black compost.[68] A list of published standards is presented in Table 7 below and one of the important standards in the list is, EN 13432. The standard provides guidelines for evaluating biodegradability and compostability and for the determination of potential harmful material constituents in packaging and packaging materials. It is mandatory that any packaging product, which is labelled as “degradable” has to be assessed using EN 13432, to ensure its compliance to EU directive on Packaging and Packaging Waste (94/62/EC).

Any toxicity effects of biodegraded metabolites of plastic can have an adverse effect on animal life, plant germination and growth. Therefore, it is necessary to assess any such effects on those species due to presence of residual plastic species and metabolites. Animal and plant toxicity is carried out using earthworms (as a representative of soil organisms), Daphnia (as a representative of aquatic organisms) and two higher plants (EN 13432). The toxicity test is a European test (OECD guideline #207) in which earthworms are exposed to soil and compost in varying amounts. Following 14 days of exposure, the number of surviving earthworms is counted and weighed and the percent survival rate is calculated. In the acute toxicity test, earthworms are exposed to high concentrations of the test material for short periods of
time. Compost worms (*Eisenia fetida*) are used for testing, as they are very sensitive to metals such as tin, zinc, heavy metals and high acidity. The Daphnia toxicity test can establish whether degradation products present in liquid medium pose any problem to surface water bodies. In the test, Daphnia are placed in test solutions for 24 h. After exposure, the number of surviving organisms is counted and the percent mortality is calculated. In plant toxicity tests, seeds are germinated in soil/compost containing degraded plastic products for a specific period (as specified in EN 13432). At the end of the test, the germination numbers (number of sown plants) and the plant biomass of the sample compost and the blank compost are compared at all mixing rates and the results are used to determine the toxic effect of biodegraded plastic products.

Bonora and Corte[115] demonstrated that degraded polyethylene containing ENVIRON additives were not hazardous (norm EC OJL, 219, 7.8.98 for soil improvers) and are non-toxic (Daphnia magna, Immobilization tests acc to ISO 6341; Earthworm, acute toxicity test acc to ISO 11268-1; Cress test acc to ISTA; Oat and lentils test acc to ISO 11269-2). However, there is no mention that additives pass the test standard EN 13432 requirements.

9 Sample Characterization

9.1 Carbonyl index

Fourier Transform Infrared (FTIR) spectroscopy is widely used in studying the oxidation of polymers. The extent of oxidation can be determined by measuring the levels of ketone and ester carbonyl absorbance peaks.
Typically, the absorbance peak for the ketone carbonyl is observed at 1715 cm\(^{-1}\) and the ester carbonyl at 1735 cm\(^{-1}\). The carbonyl index is calculated by taking the ratio of the carbonyl absorbance to the absorbance of the C-H stretching at 1465 cm\(^{-1}\), which remains essentially unchanged during oxidation.[7, 116] This provides a means of quantifying the oxidative degradation over time. In the case of oxo-biodegradable polymers it would be typical to see an increase in carbonyl index, followed by a decrease in carbonyl index during the biodegradation stage.

9.2 Molecular weight

Gel Permeation Chromatography (GPC) is frequently used to determine molecular weights of polymers and plastics.[112] The technique allows determination of number-average molecular weight (\(M_n\)), mass-average molecular weight (\(M_w\)), and polydispersity (\(M_w/M_n\))/molecular weight distribution of a wide range of polymers.

GPC analysis is necessary for structural analysis as well as to track rate of degradation of polymers under range of physical, chemical and biological conditions.

10 Summary and Conclusions

The use of plastics, especially polyolefins has increased significantly in recent decades due largely to their low cost, good mechanical properties and light weight. However, this increase in usage has also created disposal problems. Traditional disposal methods include recycling, incineration and burying in
landfill. Since polyolefins do not easily degrade in the natural environment, the need for degradable polyolefins has become a major topic of research in order to manage such environmental problems. The aim of degradable polyolefin design is to retain functionality as a commodity plastic for the required service life but degrade to non-toxic end products in a disposal environment.

Degradable polyolefin systems are typically designed to oxo-degrade undergoing changes in chemical structure as a result of oxidation in air, causing the breakdown of the molecules into small fragments that are then bioassimilated.

This paper has provided an overview of the current technologies available for producing degradable polyolefins as well as the standard test methods for evaluating degradation. It is hoped that this review has provided a sound understanding of the typical prodegradant additives used and the mechanisms by which they control degradation.

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$\text{ROOH} + \text{M}^+ \rightarrow \text{RO}^* + \text{HO}^- + \text{M}^{2+}$

$\text{ROOH} + \text{M}^{2+} \rightarrow \text{ROO}^* + \text{H}^+ + \text{M}^+$

$2\text{ROOH} \rightarrow \text{RO}^* + \text{ROO}^*$

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![Structure of citric acid](image)

**Figure 4.** Structure of citric acid

![Structure of oleamide](image)

**Figure 5.** Structure of oleamide.
Figure 6. Structure of ferrocene.

Figure 7. Structure of acetyl acetonate.

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Figure 9. Structure of oleate (C₁₈H₃₄O₂).

Figure 10. Structure of dithiocarbamate.

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Figure 37. SEM micrographs of LDPE/starch: 75/25 (a) untreated; (b) after soil burial for 6 months; (c) after exposure to UV – sunlight for 60 days followed by soil burial treatment for 6 months. [99]
Figure 38. Biological oxidation and hydrolysis by enzymes.[124]
Figure 39. Proposed mechanism for the biodegradation of polyethylene.[100, 125]

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<thead>
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<th>Tradename</th>
<th>Manufacturer</th>
<th>Active Components</th>
<th>Loadings (%wt)</th>
<th>Degrading Conditions</th>
<th>Polymer Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDPA</td>
<td>EPI</td>
<td>Metal stearates (Fe, Ce, Co) &amp; citric acid (typically Co)</td>
<td>2-3</td>
<td>Yes</td>
<td>PP, PE, PS</td>
</tr>
<tr>
<td>Renatura</td>
<td>Nor-X Industries</td>
<td>Iron stearate &amp; combination of stabilisers/antioxidants</td>
<td>2</td>
<td>Yes</td>
<td>PP, PE</td>
</tr>
<tr>
<td>Reverte</td>
<td>Wells Plastics Limited</td>
<td>Undisclosed photo-inhibiting package, metal ion prodegradant package &amp; biodegradation promotors (micronised cellulose).</td>
<td>1-5</td>
<td>Yes</td>
<td>PP, PE, PS, PET, ABS</td>
</tr>
<tr>
<td>AddiFlex</td>
<td>Add-X Biotech</td>
<td>Metal carboxylate (Fe, Mn, Cu, Co, Ni), starch, CaCO₃; Manganese stearate has been identified for AddiFlex HE[61]</td>
<td>10-20 (AddiFlex A) 1-3-6 (AddiFlex HE) 1.5-6 (AddiFlex HES)</td>
<td>Yes</td>
<td>PP, PE, PS</td>
</tr>
<tr>
<td>d₂W</td>
<td>Symphony Environmental</td>
<td>Metal stearates &amp; stabilisers (typically Mn)</td>
<td>1-3</td>
<td>NA</td>
<td>PP, PE</td>
</tr>
<tr>
<td>Scott-Gilead technology</td>
<td>Metal dithiocarbamate</td>
<td></td>
<td></td>
<td>No</td>
<td>PP, PE</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Long-term stabiliser</th>
<th>Useful lifetime(^1) (days)</th>
<th>Lifetime(^2) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.5-1</td>
<td>3-4</td>
</tr>
<tr>
<td>UV absorber</td>
<td>2-4</td>
<td>6-12</td>
</tr>
<tr>
<td>Phenolic antioxidant</td>
<td>2-3</td>
<td>4-8</td>
</tr>
<tr>
<td>Hindered amine, low M(_w)</td>
<td>8-10</td>
<td>20-25</td>
</tr>
<tr>
<td>Hindered amine, high M(_w)</td>
<td>40-45</td>
<td>60-70</td>
</tr>
</tbody>
</table>

\(^1\) Useful lifetime: defined as time period in which the tensile strength is greater or equal to 50% of the original value.

\(^2\) Lifetime: defined as the time period in which the tensile strength is less than 10% of the original value.
<table>
<thead>
<tr>
<th>Source</th>
<th>Sample type</th>
<th>Microorganisms</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Culture collection</td>
<td>LDPE w/o prooxidants</td>
<td><em>Gliocladium virens</em> ATCC 9645</td>
<td>[126]</td>
</tr>
<tr>
<td></td>
<td>thermal and/or UV pre-treatment</td>
<td><em>Aspergillus niger</em> ATCC 9642</td>
<td>[89, 126]</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Penicillium pinophilum</em> ATCC 11797</td>
<td>[89, 126]</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Phanerochaete chrysosphorium</em> H289</td>
<td>[126, 127]</td>
</tr>
<tr>
<td>Culture collection</td>
<td>LLDPE w/6% starch prooxidant</td>
<td><em>Phanerochaete chrysosporium</em> ME 446</td>
<td>[108]</td>
</tr>
<tr>
<td></td>
<td>POLYCLEAN®</td>
<td><em>Streptomyces viridosporous</em> ATCC 39115</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UV and thermal pre-treatment</td>
<td><em>Streptomyces badius</em> ATCC 39117</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Streptomyces setonii</em> ATCC 39116</td>
<td></td>
</tr>
<tr>
<td>Culture collection</td>
<td>LDPE, LLDPE w/cobalt acetylacetone</td>
<td><em>Aspergillus niger</em> ATCC 6275</td>
<td>[128]</td>
</tr>
<tr>
<td></td>
<td>Thermal pre-treatment</td>
<td><em>Gliocladium virens</em> ATCC 9645</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Paecilomyces variotii</em> 10121</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Penicillium funiculosum</em> ATCC 19010</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Streptomyces</em> strain</td>
<td></td>
</tr>
<tr>
<td>Culture collection</td>
<td>LDPE w/prooxidant</td>
<td><em>Pseudomonas aeruginosa</em></td>
<td>[6]</td>
</tr>
<tr>
<td>Culture collection</td>
<td>HDPE</td>
<td><em>Phanerochaete chrysosphorium</em></td>
<td>[87]</td>
</tr>
<tr>
<td>Culture collection</td>
<td>LDPE Fe prooxidant</td>
<td><em>Cladosporium cladosporioides</em> ATCC 20251</td>
<td>[54, 129]</td>
</tr>
<tr>
<td></td>
<td>TDPA® prooxidants from EPI</td>
<td><em>Rhodococcus rhodochrous</em> ATCC 29672</td>
<td></td>
</tr>
<tr>
<td>Condition</td>
<td>Treatment</td>
<td>Organism</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>----------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Rubber degrading</td>
<td>thermal &amp; UV pre-treatment</td>
<td><em>Nocardia asteroides</em></td>
<td></td>
</tr>
<tr>
<td>Culture collection</td>
<td>PE w/6wt% starch thermal pre-treatment</td>
<td><em>Mucor rouxii</em> 1835</td>
<td>[130]</td>
</tr>
<tr>
<td>Laboratory isolate</td>
<td></td>
<td><em>Aspergillus flavus</em></td>
<td></td>
</tr>
<tr>
<td>Paraffin wax degrading</td>
<td>LDPE w/ starch/Fe stearate thermal pre-treatment and</td>
<td><em>Arthrobacter paraffineus</em></td>
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<tr>
<td></td>
<td>LDPE w/ starch, Mn stearate, w/ styrenbutadiene co-polymer thermal pre-treatment</td>
<td></td>
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</tr>
<tr>
<td>Soil</td>
<td>LDPE w/photosensitizer thermal and UV pre-treatment</td>
<td><em>Rhodococcus rubber</em></td>
<td>[88]</td>
</tr>
<tr>
<td>Soil</td>
<td>LDPE w/photosensitizer thermal and UV pre-treatment</td>
<td><em>Brevibacillus borstelensis</em></td>
<td>[95]</td>
</tr>
<tr>
<td>Soil</td>
<td>HDPE UV &amp; thermal pre-treatment with nitric acid</td>
<td><em>Penicillium simplicissimum YK</em></td>
<td>[79]</td>
</tr>
<tr>
<td>Soil</td>
<td>LDPE w/prooxidant UV and thermal pre-treatment</td>
<td><em>Rhodococcus sp</em></td>
<td>[83]</td>
</tr>
<tr>
<td>Soil</td>
<td>LDPE w/60% Bionella thermal pre-treatment</td>
<td><em>Aspergillus niger</em></td>
<td>[132]</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Penicillium funiculosum</em></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>LDPE w/cobalt stearate UV pre-treatment</td>
<td><em>Bacillus pumilus</em></td>
<td>[85]</td>
</tr>
</tbody>
</table>

100
<table>
<thead>
<tr>
<th>Marine</th>
<th>LDPE and HDPE</th>
<th>Bacillus cereus GC subgroup IV [133]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpretreated &amp; thermal treatment</td>
<td>Bacillus cereus subgroup A</td>
<td></td>
</tr>
<tr>
<td>Unpretreated &amp; starch-blended</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Laboratory isolate</th>
<th>LDPE thermal pre-treatment</th>
<th>Rhodococcus ruber [92]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE wax</td>
<td></td>
<td>Bacterial consortium KH-12 [80]</td>
</tr>
</tbody>
</table>

PE, polyethylene; LDPE, low density polyethylene; HDPE, high density polyethylene; LLDPE, linear low density polyethylene; w, with; w/o, without; UV, ultraviolet radiation
Table 4. List of published standards for photodegradation.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D6954 – 04</td>
<td>Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation.</td>
</tr>
<tr>
<td>ASTM D4329 – 05</td>
<td>Standard practice for fluorescent UV exposure of plastics</td>
</tr>
<tr>
<td>ASTM D5071 – 99</td>
<td>Standard practice for exposure of photodegradable plastics in a xenon arc apparatus</td>
</tr>
<tr>
<td>ASTM D5208 – 01</td>
<td>Standard practice for fluorescent ultraviolet (UV) exposure of photodegradable plastics</td>
</tr>
<tr>
<td>ISO 877:1994</td>
<td>Plastics – Methods of exposure to direct weathering, to weathering using glass-filtered daylight, and to intensified weathering by daylight using Fresnel mirrors.</td>
</tr>
<tr>
<td>ISO/CD 10640 (under development)</td>
<td>Plastics – guidance on the assessment of accelerated photo ageing</td>
</tr>
</tbody>
</table>
Table 5. List of published Standard for thermal ageing.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D6954 – 04</td>
<td>Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation.</td>
</tr>
<tr>
<td>ASTM D3045 – 92</td>
<td>Standard practice for heat aging of plastics without load</td>
</tr>
<tr>
<td>ISO 4577:1983</td>
<td>Plastics; Polypropylene and propylene – copolymers; Determination of thermal oxidative stability in air; Oven method</td>
</tr>
<tr>
<td>Standard</td>
<td>Description</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>ASTM D6954 – 04</td>
<td>Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation.</td>
</tr>
<tr>
<td>AS 4736 – 2006</td>
<td>Biodegradable plastics – biodegradable plastic suitable for composting and other microbial treatment</td>
</tr>
<tr>
<td>ASTM D5209 – 92</td>
<td>Standard test method for determining the aerobic biodegradation of plastic materials in the presence of municipal sewage sludge</td>
</tr>
<tr>
<td>ASTM D5338 – 98</td>
<td>Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions</td>
</tr>
<tr>
<td>ASTM D5951 – 96</td>
<td>Standard practice for preparing residual solids obtained after (2002) biodegradability standard methods for plastics in solid waste for toxicity and compost quality testing</td>
</tr>
<tr>
<td>ASTM D5988 – 03</td>
<td>Standard test method for determining aerobic biodegradation in soil of plastic materials or residual plastic material after composting</td>
</tr>
<tr>
<td>ASTM D6002 – 96</td>
<td>Standard guide for assessing the compostability of environmentally degradable plastics</td>
</tr>
<tr>
<td>ASTM D6340 – 98</td>
<td>Standard test methods for determining aerobic biodegradation of radiolabeled plastic materials in an aqueous or compost environment.</td>
</tr>
<tr>
<td>ASTM D6400 – 99</td>
<td>Standard specifications for compostable plastics</td>
</tr>
<tr>
<td>ASTM D6691 – 01</td>
<td>Standard test method for determining aerobic biodegradation of plastic materials in the marine environment by a defined microbial consortium</td>
</tr>
<tr>
<td>ASTM D6692 – 01</td>
<td>Standard test method for determining biodegradability of radiolabeled polymeric plastic materials in seawater</td>
</tr>
<tr>
<td>ASTM D7081 – 05</td>
<td>Standard specifications for non-floating biodegradable plastics in the marine environment</td>
</tr>
<tr>
<td>DIN V 54900-2</td>
<td>Testing of compostability of plastics – part 2: testing of the complete biodegradability of plastics in laboratory tests</td>
</tr>
<tr>
<td>EN 13432:2000</td>
<td>Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging</td>
</tr>
<tr>
<td>EN 14045:2003</td>
<td>Packaging – evaluation of the disintegration of packaging materials in practical oriented tests under defined composting conditions.</td>
</tr>
</tbody>
</table>

EN 14806:2005 Packaging – preliminary evaluation of the disintegration of packaging materials under simulated composting conditions in a laboratory-scale test.

ISO 14851:1999 Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – method by measuring the oxygen demand in a closed respirometer.


ISO 14855:1999 Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions – method by analysis of evolved carbon dioxide.

ISO 14593:1999 Water quality – evaluation of the ultimate aerobic biodegradability of organic compounds in aqueous medium – method by analysis of inorganic carbon in sealed vessels (CO$_2$ headspace test)

ISO 15314:2004 Methods for marine exposure

ISO 16221:2001 Water-quality – guidance for the determination of biodegradability in the marine environment

ISO 16929:2002 Plastics – determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test.

ISO 17556:2003 Plastics – determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved.

ISO 20200:2004 Plastics – determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test.

CEN/TR 15822 Plastics- biodegradable plastics in or on soil – Recovery, disposal and (under approval) related environmental issues
Table 7. List of published standards which include eco-toxicity.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Description</th>
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<tbody>
<tr>
<td>ASTM D5951 – 96</td>
<td>Standard practice for preparing residual solids obtained after biodegradability standard methods for plastics in solid waste for toxicity and compost quality testing.</td>
</tr>
<tr>
<td>ASTM E1676 – 04</td>
<td>Standard guide for conducting laboratory soil toxicity or bioaccumulation tests with the lumbricid earthworm <em>Eisenia fetida</em> and the enchytraeid potworm <em>Enchytraeus albidus</em>.</td>
</tr>
<tr>
<td>EN 13432:2000</td>
<td>Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging.</td>
</tr>
</tbody>
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