ENVIRONMENTALLY DEGRADABLE PLASTICS BASED ON OXO-BIODEGRADATION OF CONVENTIONAL POLYOLEFINS

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BIOGRAPHICAL NOTE

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ABSTRACT

Polyolefins are the best choice for many film applications, because they are cheap, easy to process, tough and bio-inert. Additives can now be incorporated into polyolefins to accelerate degradation, with lifetime control. Films containing commercial additives have been aged in ovens, in UV and outdoors. Oxidation and loss of molecular weight are accelerated and degradation can be controlled by the choice of additive. The polymers become extremely brittle and hydrophilic. The degraded films are biodegradable in composting and soil burial and no harmful effects could be detected in ecotoxicity tests. Mineralization tests show rapid colonization of the oxidised polymers by microorganisms and high conversions to CO_2 over timescales compatible with intended applications.

INTRODUCTION

The synthetic plastics industry has been one of the great industrial successes of the last 50 years, transforming everyday life in a multiplicity of ways. Although not always appreciated as such, it is an extremely “green” industry. The manufacture of thermoplastics converts light oil fractions which would otherwise be flared into lightweight plastics. In essentially every life cycle analysis of plastics in comparison with other materials in e.g. packaging, the use of plastic demonstrably leads to major savings in energy, weight and pollution [1]. Newer developments in catalysis are steadily improving the position as better control of molecular weight distribution, stereoregularity and branching give plastics (especially polyolefins) with better processing characteristics and mechanical performance, allowing thinner films and reducing the weight of plastic articles. Among the numerous applications for commodity thermoplastics, films and moulded containers are very important. Polyethylene (PE) and polypropylene (PP) are commonly used because of their low cost, easy processing and good mechanical properties. In addition, injection moulded materials like high-impact polystyrene (HIPS) are becoming widely used in e.g. disposable plastic cutlery.

Although extending the lifetime of plastics has dominated plastics technology in the last 50 years, there are many products that have a relatively short use life (weeks or months), following which they are no longer needed and are discarded. At this point the durability and persistence of man-made plastics become disadvantages. The downside of their success is that the amounts of plastic both in domestic and industrial wastes and in litter have increased very rapidly in recent years, creating major problems in waste disposal and leading to a demand for materials which will perform their function as well as conventional plastics yet will somehow “disappear” at the end of their useful life. As a result there has been rapid growth in the development of polymers which are either intrinsically degradable or rendered degradable by appropriate additives [2,3]. Among these, polymers which hydrolyse to biodegradable fragments have had a profound appeal to environmentalists because of the perception that they are somehow more “natural” than hydrocarbon plastics. This view has been reinforced in recent years by the developments in polymers produced directly by fermentation, or from monomers derived by fermentation.

It must be emphasised that rapid biodegradation should be the solution of last resort for the general disposal of plastics. Thermoplastic materials have intrinsic value - the material value can be recovered by reuse or recycling; they have value as chemicals – they can be pyrolysed or otherwise degraded to give useful chemicals and they have energy value – they can be burned to give heat. Although there are obvious examples where rapid biodegradation is useful and important, e.g. for biomedical applications and for products which end their lives in sewage systems, in general rapid biodegradation is simply "burning" the polymer to CO_2 and water without recovering anything. On the other hand, rapid loss of mechanical properties followed by slower biological assimilation has the virtue of providing useful biomass.

To be considered as environmentally degradable, a plastic must thus satisfy at least two requirements. On outdoor exposure or soil burial it must become brittle rapidly enough to disappear visually, and the degraded material must be susceptible to eventual biological attack giving complete conversion to biomass over an appropriate time, without release of toxic products.

For microflora (fungi, bacteria etc) to assimilate the carbon in any substrate, a number of criteria must be met. The substrate must be water–wettable, and the constituent molecules sufficiently small that a very large number of their chain ends are accessible at the surface of the material. Hydrocarbon thermoplastics are bio-inert because they are hydrophobic, and because their good mechanical properties require very high molecular weights, leading to very few accessible chain ends.

One major approach to biodegradable materials is polymers, typically aliphatic polyesters, which are hydrolysed to biodegradable fragments. These may be laboratory products, from fossil fuel or renewable feedstocks, synthesized from fermentation products, or produced directly by fermentation. Obvious examples are the poly(hydroxyalkanoate)s, produced by bacterial fermentation [4], and poly(lactic acid) (PLA) [5]. PLA, polycaprolactone (PCL) and the poly(hydroxyalkanoate)s hydrolyse under relatively mild conditions, to yield biodegradable fragments with acid or alcohol end groups. Their bio-assimilation is a synergistic interaction between hydrolysis and biodegradation (hydro-biodegradation). Despite many years of development, these plastics have yet to make major impact in the marketplace because of relatively high production costs [6].

Conventional polyolefins are still much the best solution for many applications requiring tough films, because PE and PP are cheap, easy to process and both mechanically tough and bio-inert. Although both PE and PP will degrade naturally, the timescale is too long for them to be considered environmentally "friendly" and the increasing demand for such materials requires ways of converting them into water-wettable, mechanically weak material in short periods. The solution lies in accelerating the natural oxidative degradation of the polymers. In many applications the, the target is that the properties will deteriorate quickly at the end of the useful lifetime. Finally, upon total mechanical degradation, the residual plastic should be taken up into the bio-cycle without any negative influence on the environment.

EPI Inc. has developed "Totally Degradable Plastic Additive" (TDPA®) formulations, which can be incorporated into conventional polyolefins during normal processing to induce accelerated oxidation on exposure to UV light or, more importantly, to heat. The resulting degradation leads to products which are biodegradable. This paper describes some studies and applications of these oxo-biodegradable products with emphasis on film applications in agriculture, landfill and packaging and on compostabilty and biodegradation of the products. For agricultural applications EPI formulations are developed and marketed by Ciba Specialty Chemicals, under the trade name "Envirocare™".

POLYOLEFIN OXIDATION AND ITS ACCELERATION

The mechanisms of oxidative degradation of polymers, have been extensively studied and reviewed [7]. It is generally accepted that the key intermediates are hydroperoxides, which are always present because of oxidation during preparation or processing, and decompose under the influence of heat, light or transition metal catalysis to produce free radicals. Once radicals are produced they enter a chain reaction with oxygen and C-H bonds in the polymer, to produce a range of oxidation products. This can be expressed as the interlocking cycle of reactions depicted in figure 1.

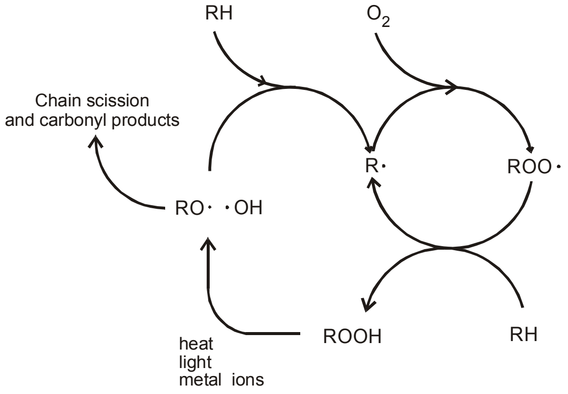

Figure 1: The interlocking cycle of reactions leading to oxidation of a polymer

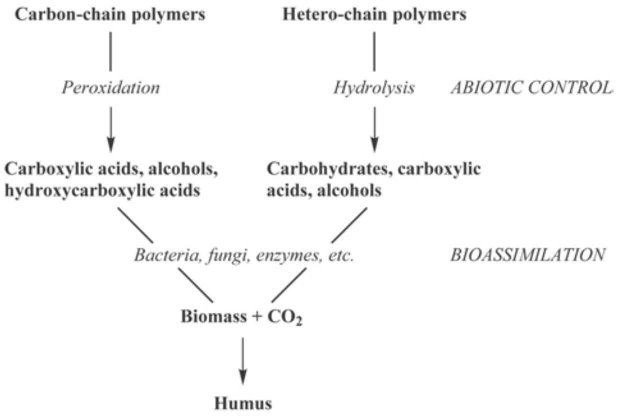

Figure 2: Biodegradation routes for oxo- and hydro-biodegradable polymers [2]

The primary products of this cycle are hydroperoxides, so that oxidation generates its own initiator and has all the characteristics of an autoaccelerating chain reaction. The decomposition of hydroperoxides yields alkoxy radicals which are responsible for many secondary products. In particular, β-elimination by alkoxy radicals competes with H-abstraction, and leads to chain scission and formation of a variety of carbonyl products. Since linear polymers derive their mechanical properties from the entanglement of their long chains, limited chain scission causes a rapid change from tough to brittle materials. This is especially true of thin films, which require plastic of extreme toughness.

Since hydroperoxide decomposition to give free radicals is the key reaction in oxidation, additives which reduce their rate of formation, or decomposition or which decompose hydroperoxides by non-radical routes will act as antioxidants. Conversely, additives which act to accelerate hydroperoxide formation and decomposition to radicals are effective pro-oxidants since they accelerate the chain branching reactions.

EPI TDPA® and Ciba Envirocare™ formulations are additives that, when compounded with conventional polymers at appropriate levels, control the formation and decomposition of hydroperoxides. Their use allows control of the lifetimes of plastic films and articles. Stability is maintained during processing, storage and short-term end use. Once the material is discarded, oxidative degradation (initiated by heat, UV light or mechanical stress in the environment) is accelerated by as much as several orders of magnitude. The oxidized molecular fragments are hydrophilic, have molar mass values reduced by a factor of 10 or more, and are ultimately biodegradable.

These products are typically incorporated into the final formulation as additives at levels of a few percent. They are proprietary combinations of additives, which, with appropriate compositional adjustments, allow for a wide range of storage, use, and degradation times, depending on the end use and the environment. Polyolefin pellets, which have been compounded with these additives, are processed on conventional equipment at normal speeds.

An important feature of these additives is that they are activated both by the action of sunlight and by heat. Thus outdoor degradation of e.g. packaging or mulch films can occur both for material that is exposed to light and for material covered by soil. Equally important is that the polymer is compatible with all normal recycling processes, although high levels of TDPA® additives in a recycle stream may require extra stabilisation.

BIODEGRADATION OF OXIDISED POLYOLEFINS

It is well known that oxidation of polyolefins leads to rapid loss of molar mass and the development of hydrophilic surfaces. Reduction of the molecular weight of PE to values around 40,000, combined with the introduction of oxygen-containing functional groups, leads to biodegradable products [8-10].

In a natural environment microorganisms colonizing a substrate form a biofilm, consisting of bacteria and fungi in a highly hydrated (85-98% water) matrix of extracellular polymers. Both hydrolysis and oxidation of the substrate can be mediated by the biofilm, by release of extracellular enzymes or free radicals. Fungi in particular can spread rapidly by secreting enzymes and free radicals. In addition, insoluble compounds that cannot cross a cell membrane are also susceptible to attack. The mycelial growth habit of fungi also gives a competitive advantage over single cells, especially in the colonization of insoluble substrates. Hyphal penetration provides a mechanical complement to the chemical breakdown, and the high surface-to-cell ratio characteristic of the growing fungi maximizes both mechanical and enzymatic contact with the environment. Cell enzymes, and particularly cytochrome P450 which is produced by many bacteria, continue peroxidation by reducing ground-state oxygen to the free radical superoxide ($O_2^{\cdot -}$). When protonated, this species is converted to the much more reactive peroxyl radical and hydrogen peroxide, which can be reduced by transition metal ions in the polymer to give the highly reactive hydroxyl radical. OH radicals initiate further peroxidation leading to continued biodegradation and ultimate bioassimilation to biomass and CO_2 as long as environmental oxygen and cell nutrients are available. Thus, the bio-assimilation of degraded polyolefins is a synergistic oxo-biodegradation (Figure 2). In that sense it is totally analogous to the two-stage, hydro-biodegradation, by which linear polyesters are microbially assimilated.

LABORATORY STUDIES OF DEGRADATION

Polyolefins compounded with EPI additives degrade rapidly in laboratory ageing. Experiments using FTIR spectroscopy, tensile testing and molecular weight measurement by size exclusion chromatography (SEC) demonstrate rapid loss of mechanical strength and chain length and formation of oxidation products [11].

Typical results from IR spectroscopy are presented in Figure 3, which shows the carbonyl region of the spectrum for two samples degraded in an air oven at 50°C for the same time under identical conditions, with and without additive. The extensive degradation of the additive-containing sample is clear from the growth of the IR bands between 1700 and 1750 cm^{-1} associated with carbonyl groups of oxidation products.

Figure 4 [12] shows failure data for samples of a transparent LLDPE film formulated with Envirocare™ additives for use in agricultural mulching, and exposed in a circulating air oven at 50°C. Failure was taken as the time to embrittlement of the film (typically it crumbles to powder when handled, implying that the elongation to break has fallen to less than 5% of its original value); it can be varied by choosing the appropriate amount and composition of the additive and can be accelerated significantly and controllably.

Figure 5 shows data for samples of PE film exposed to artificial UV ageing in a Xenon weatherometer [12]. The lifetime to embrittlement of transparent films can be reduced significantly by the appropriate additive. Addition of carbon black to unmodified film produces a major stabilizing effect, which can easily be overcome by the additive.

It is important to emphasize that the TDPA® and Envirocare™ additive packages do not change the mechanism or products of the degradation of polymers. They simply accelerate the normal reactions, leading to the same final products in shorter times.

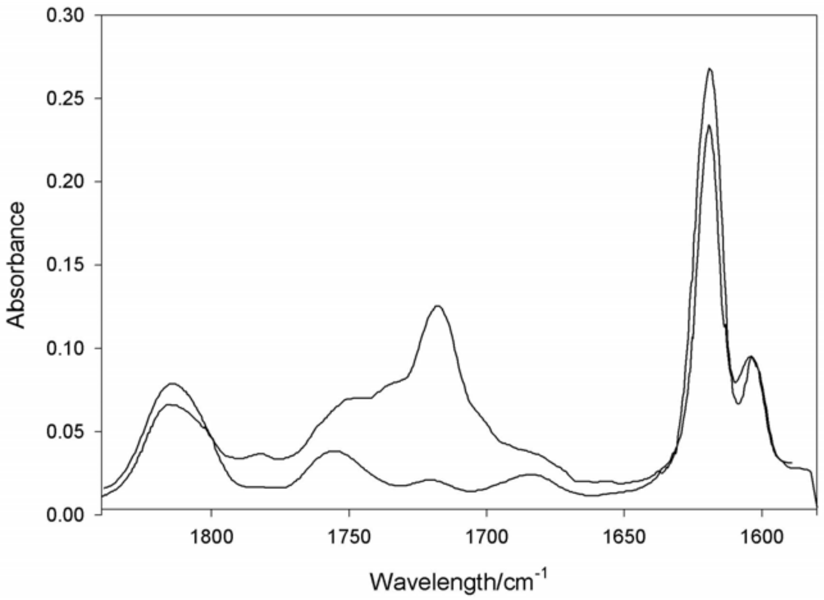

Figure 3: FTIR spectra of PP films after air-oven ageing without (lower trace) and with (upper trace) additive.

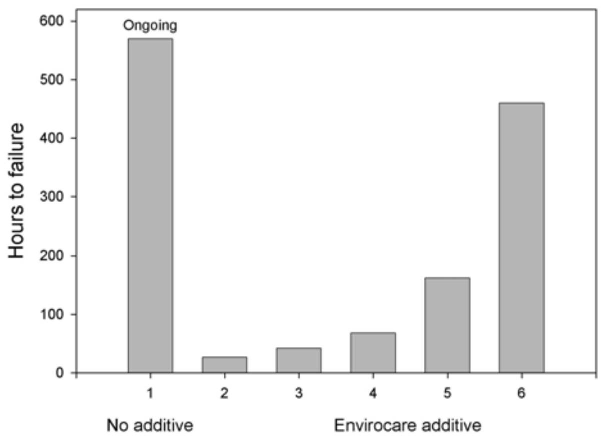

Figure 4: Performance of Envirocare™ systems in long term heat ageing. 25 μm LLDPE [12]

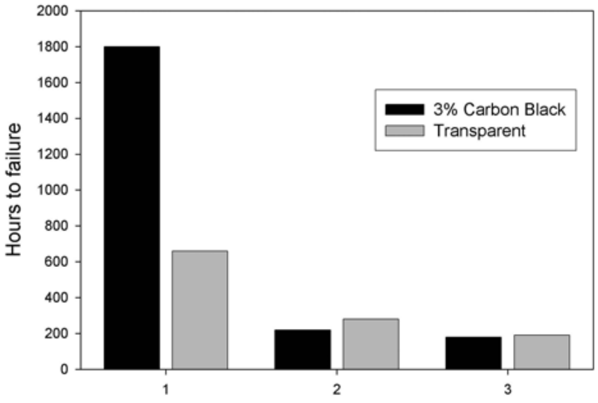

Figure 5: Performance of Envirocare™ additives in UV ageing of 25 μm LLDPE film with and without carbon black (3 wt%). Exposure: WOM (BPT: 63 ± 3°C) [12]

APPLICATIONS OF OXO-BIODEGRADABLE PLASTICS

Polyolefins and other polymers destabilized with TDPA® and Envirocare™ additives are finding applications in many areas. Two important ones are illustrated here; agricultural mulching films and litter and landfill management.

Agricultural Applications

A particularly good application of degradable plastics is as agricultural films, which are widely used in the form of mulch and silage films, to improve crop cultivation and protect agricultural products after harvesting. Around 2.8 million tonnes of agricultural plastics are consumed annually world-wide and cover more than 5 million hectares of land. The majority of this surface is covered by mulch film, accounting for 4.5 million hectares. Mulch films are extensively used to modify soil temperature, limit weed growth, prevent moisture loss, and improve crop yield. For example, Figure 6 shows the example of melons grown through a degradable mulch film. The film not only limits weed growth and conserves moisture and fertilizer, it also keeps the crop from direct soil contact and gives a much higher quality product.

Like all plastics, ordinary PE mulch films undergo photo/thermal oxidation characterized by a steady decline in physical properties. As a result, they may fail to protect the growing crops for a sufficiently long period. Conversely, pigments and stabilizers can provide a long service life but the mechanical breakdown at the

Figure 6: Melon grown through degradable LLDPE mulch film
(Photo courtesy of Trioplast Ltd)

end of the growing season may be too slow for convenience in cultivation and re-cropping. Collection and recycling of used film has been found to be impractical but it cannot be left on the fields as it interferes with mechanical harvesting. The use of prodegradants allows all of the advantages of PE to be retained in a product which loses its mechanical integrity at the end of the growing season. There is extensive experience over very many years in the use of degradable polyolefins in agricultural mulching [13,14], though mostly with photodegradable films; a particular advantage of Envirocare™ materials is that they are activated by both heat and light.

An obvious problem is that different crops have different lengths of growing season and different locations have different soil temperatures and receive different amounts of sunlight. The great advantage of the additive approach is that with a knowledge of the growth conditions plus experience in formulation it is possible to "tune" the additive package to control the lifetime. Many different Envirocare™ films have been evaluated in the Application Centre of Ciba SC in Bologna, Italy, where the variables that affect the film durability have been simulated [12]. Figure 7 shows that, by appropriate selection of additive, it is possible to achieve film lifetimes to embrittlement ranging from 30 days (or less than 20 kLys) upwards.

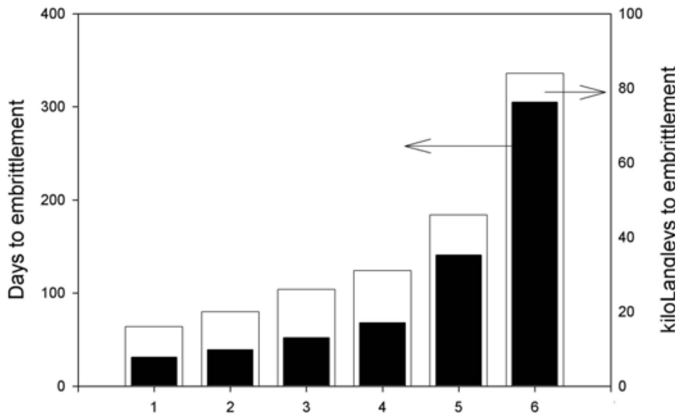

Figure 7: Embrittlement times for LLDPE mulch film with different Envirocare™ additives exposed outdoors in soil contact Italy (110 kLy yr^{-1}). Data are times (dark bars) and absorbed energy (light bars) for embrittlement. [12]

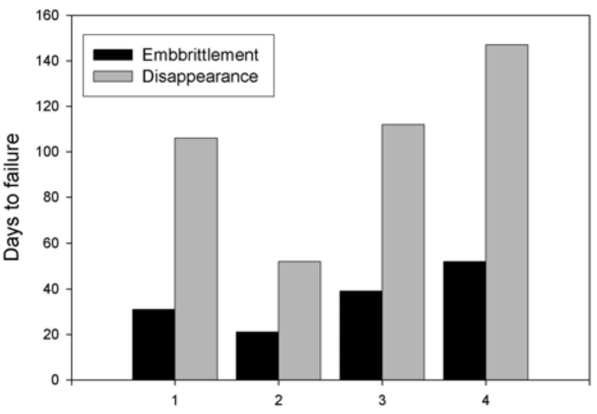

Figure 8: Embrittlement and disappearance times for LLDPE films with different Envirocare™ additives exposed in soil contact in Italy (110 kLy yr^{-1}) [12].

Figure 8 [12] shows the times to embrittlement and complete visual disappearance for some mulch films. The latter range between less than two months up to several months, depending on the additive formulation.

Mulch films containing Envirocare™ additives have been tested extensively in field trials in different countries and for different crops. Successful results have been obtained for maize, melons and cotton. Field trials of films with longer required lifetime are ongoing for crops like strawberries (6-10 months), pineapple (10 months), tomato (6 months) and watermelon (6 months). In addition to mulch films, other agricultural applications where the use of Envirocare™ additive is beneficial have been identified. Hence field trials are running in solarization films, small tunnel films, seeding bags and banana bags.

Another application for degradable plastics is in the bulk collection of green waste for commercial composting. Large-scale composting operations are well established in many countries, and are an efficient way of producing useful material from what at present is largely garden and agricultural waste. The ASTM definition of compostable is "capable of undergoing biological decomposition in a compost site as part of an available program, such that the material is not visually distinguishable and breaks down into carbon dioxide, water, inorganic compounds, and biomass, at a rate consistent with known compostable materials."

It is a mistake to think that one can emulate commercial composting conditions by enclosing vegetable and garden scraps in a plastic garbage bag in the garden. Commercial composting involves large windrows that are turned and watered to ensure that mesophilic and thermophilic microorganisms are active. Temperatures in these windrows routinely may exceed 70°C for some days, and are above 60°C for weeks. Such conditions are essential for the generation of biomass and for the conversion of the organic material in the feed into the humic materials that provide the nutritive value to the compost product. Such conditions cannot normally be obtained in back-garden composting.

Compost bags made using the appropriate grade of TDPA® PE have been proven to be excellent one-way containers for collecting and transporting compostable wastes. Degradability of PEs modified by TDPA® and

Envirocare™ additives in composting has been assessed by a variety of laboratory-scale and field-scale composting tests. Most recently an extensive commercial-scale composting trial of TDPA® additives has been carried out in the municipal composting plant of Vienna Neustadt, Austria, directed by Dr B Raninger (Leoben University). This plant serves a population of about 100,000 people. It typically treats about 10,000 tons of mixed household and green garden waste annually. Composting occurs in two stages: an in-vessel, forced aeration "tunnel" process, followed by an outdoor, open-pile windrow composting stage. The compost produced is used mainly for landscaping and gardening. Full details of this trial have been reported [15]. In essence, PE bags modified with TDPA® were included into the composting stream at a realistic level (1.1wt%) for bags in a commercial composter. Samples of the final compost were subjected to standard ecotoxicity tests, including seed germination and survival of daphnia and earthworms and were carried out according to DIN V 54900-3, ON S 2200 and ON S 2023. The results all show that PE films modified by our additives yield high-quality compost. No toxic effects could be detected on either seed germination or organism survival.

Landfill Management

It is incorrect to assume that very little of anything actually degrades in a landfill. About 50% of the municipal solid waste dumped in landfills is biodegradable. Even in modern so-called sanitary landfills, biodegradation goes on constantly. Just as in a compost heap, the organic material undergoes aerobic biodegradation, forming carbon dioxide and water, as long as oxygen and moisture are present. As the layers of waste build up, and air and water no longer penetrate from above, anaerobic bioconversion takes over, and the carbon in the waste is mostly converted very much more slowly to methane. The waste shifts and compacts, from a combination of pressure from above and bioconversion below. Normally this consolidation continues for many years, frequently decades, even after filling and capping. Together with the continuous formation of methane, which is flammable and explosive in mixtures with air, this severely restricts further use of the site. It is much better to encourage aerobic biodegradation of food, garden waste and paper to produce carbon dioxide (instead of methane) because carbon dioxide is 24.5 times less potent as a greenhouse gas than methane. It is also required for and consumed in photosynthesis, and it does not burn or explode.

The vastly increased use of PE bags as liners for kitchen bins and household dustbins exacerbates the problems of landfill re-use. When food and garden wastes are wrapped in PE films or bags, the flow of gases and liquids through the waste is prevented. Restrictions in the supply of water and air to the enclosed waste means that the rates of biodegradation of organic waste are slow, and become slower at lower levels as the essentials for aerobic microbial growth (water and oxygen) are depleted. The microbes (largely anaerobic bacteria) that begin to proliferate under anaerobic conditions are much slower acting than are the vastly greater numbers of aerobic fungi and bacteria that can biodegrade the waste when water and air are available. Rapid aerobic compaction is restricted and the period during which the biodegradation occurs to produce methane is massively prolonged. This, in turn, postpones (for years) the stabilization of the site for any other subsequent use. For both environmental and practical reasons encouragement of aerobic over anaerobic degradation is entirely preferable. It is entirely appropriate to use conventional PE for its durability and barrier properties in containing leachates, for example and preventing leakage into the water table. It is just as appropriate, however, to use oxo-biodegradable plastic for shopping bags, bin liners food wraps and other packaging materials.

Another environmentally beneficial use for degradable PE is as daily cover for landfills. The correct operation of a sanitary landfill requires that a cover be applied to the "active face" at the end of operations each day. This is to prevent the wind, birds, rodents, etc. from causing visual problems by scattering rubbish around the countryside. It is also to prevent the spread of odours and hazardous materials from the top layers. Commonly several cm of soil or other bulky and/or expensive material is applied daily. This is a waste of space and/or money. TDPA® PE film provides an inexpensive but effective daily landfill cover, with a negligible volume. Within the first year it will disintegrate to assist in relatively rapid aerobic degradation of the biodegradable material in the landfill.

Several studies of the behaviour of TDPA® PE film in landfill have been reported [11,16]. All show clear evidence that microbially-generated heat in a landfill site (30 – 55°C) is enough to lead to oxidative embrittlement of polyethylene containing prodegradant, within a few months.

More recently, a large scale trial has been conducted at a commercial landfill site near Birmingham, UK over the period January 2001 – March 2002. Samples of LDPE film with and without prodegradant were laid over the surface of the landfill then buried in normal municipal waste to a final depth of 3m. During the test period, the weather was generally poor and the temperature recorded by thermocouple probes close to the test films rarely exceeded 30°C. The maximum temperature recorded was 38°C in November 2001, due to the combination of the heat from summer sunshine and the microbial activity it promotes.

Figure 9 shows samples of test films recovered from the landfill after 10 months of burial. Reliable tensile testing was impossible because of the difficulty in recovering material which had not been stretched and torn by the compaction of landfill above it. However, the control film (left) was easily recovered as a tough material. In contrast, the treated film (right) was very variable in properties but mostly extremely difficult to recover, being brittle and fragmented. Table 1 shows some comparative data for the two materials.

Table 1 Properties of LDPE film with and without TDPA® additive, before and after 10 months landfill burial

Sample	MFI /g/10min[a]	$A_{C=O}$[b]	M_w[c]
Control unburied	0.75	0	114,000
Control recovered	1.11	0.15	107,000
TDPA unburied	0.76	0	115,000
TDPA recovered	13.3	2.31	4250

a: Melt flow index according to ASTM D1238
b: Infra-red absorbance at 1715 cm^{-1}
c: Weight average molecular weight measured by GPC

These results clearly confirm the earlier conclusions that polyolefins can be made sufficiently unstable with appropriate additives that they degrade to embrittlement in an acceptable time even in a cold landfill.

ULTIMATE BIODEGRADATION OF OXIDISED FILMS

Although it is clear that appropriate additives can accelerate the oxidation of polyolefins to the point that they are mechanically destroyed, the frequently asked question is what is the ultimate fate of the degraded residues? Many earlier studies [8-10] have shown that PE which is degraded to the level indicated by our studies is biodegradable in that colonisation of the oxidised film by micro-organisms, formation of biodegradable material by oxidation, and conversion of substrate carbon to carbon dioxide have all been shown [8-10,17]. Although there is absolutely no scientific reason to expect these clearly demonstrated processes to stop, some critics have argued that only complete conversion to CO_2 in times comparable to e.g. cellulose can be accepted as a definition of biodegradability.

A major problem for all studies of biodegradation of polymers is the lack of clear, unambiguous and generally acceptable standards for defining or testing biodegradability. The superficially simple problem is fraught with hazards. All organic materials are biodegradable in some timescale, though complete conversion to CO_2 and water (mineralisation) may take centuries. Tests which require complete conversion of organic carbon to CO_2 in short periods (such as are currently being proposed by many bodies, like ASTM and CEN) can be counter-productive since a) many materials commonly recognized as biodegradable, like much plant tissue, will fail such tests and b) it is far more sensible for the organic carbon to be converted into useful biomass rather than released as greenhouse gases.

Manufacturers and users of oxo-biodegradable polyolefins view with concern the development of standards for degradable polymers which demand a high level of mineralisation as the primary criterion. This protocol was originally developed for hydro-biodegradable polymers, which will primarily end up in sewage. For these polymers and in this application, such test methods are entirely acceptable but they are totally inappropriate for compost, litter and agricultural applications.

Because of these problems, a number of recent studies have been published, both of EPI materials and of related products. In one of the most recent, Jakubowicz [18] studied thermo-oxidative degradation of PE films containing a pro-oxidant, at three temperatures normal for composting. It was shown that the material is bioassimilated once it is oxidatively degraded. The rate of aerobic biodegradation of the oxidation products was evaluated under controlled composting conditions using measurements of carbon dioxide production. The degree of bioassimilation was about 60%, and was still increasing, after 180 days.

In another new study [19], samples of PE film modified with TDPA® additives were oxidized by oven ageing, and the fragments incubated with cultures of a bacterium (*Rhodococcus rhodochrous*) or a fungus (*Cladosporium cladosporoides*). It was observed that microbial growth occurred even on PE samples that had been compression moulded but not deliberately pre-oxidised. Figure 10 is an SEM micrograph of the surface of an oxidized sample incubated with the bacterium. The colonization and erosion of the polymer surface are both clear. There was clear evidence from photo-acoustic FTIR, which measures changes in the surface of the polymer, that proteins and polysaccharides, associated with the growth of microoganisms at the expense of the polymer oxidation products, are both formed on the surface of the polymer. After removal of the microorganisms, the surface was pitted, eroded and physically weak.

In another study [20], PE samples containing TDPA® pro-oxidant additives have been subjected to respirometric (CO_2 evolution) tests aimed at simulating soil burial and composting (mature compost) conditions. Retrieved degradation specimens, their solvent extracts and residues were also tested in soil burial respirometric tests to evaluate their potential biodegradability. TDPA® LDPE samples were found to undergo biodegradation, mediated by soil microorganisms, in respirometric experiments. High mineralisation levels were observed, approaching 60 % and comparable to those occurring in the case of several natural polymers in natural environments, as shown for example in figure 11. Compared to more conventionally biodegradable materials, such as cellulose, the time for biodegradation is relatively longer. However, it is clear from the positive biodegradation profile that biodegradation continues. Degradation is accompanied by a dramatic change in the structural characteristics of the test samples.

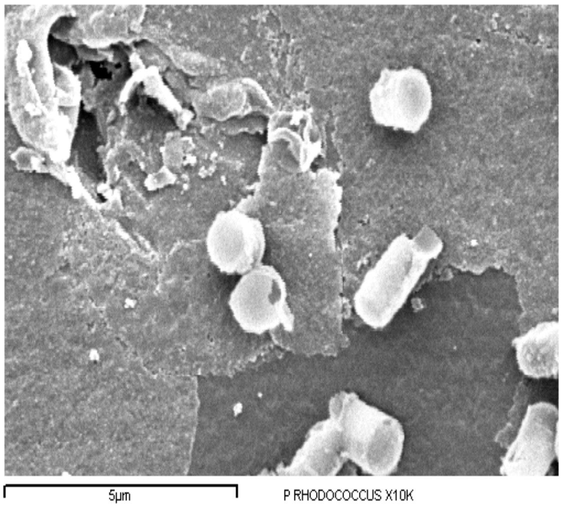

Figure 10: Bioerosion of peroxidised PE and the growth of *Rhodococcus rhodochrous* observed by SEM after 1 month (reproduced with permission of the authors)

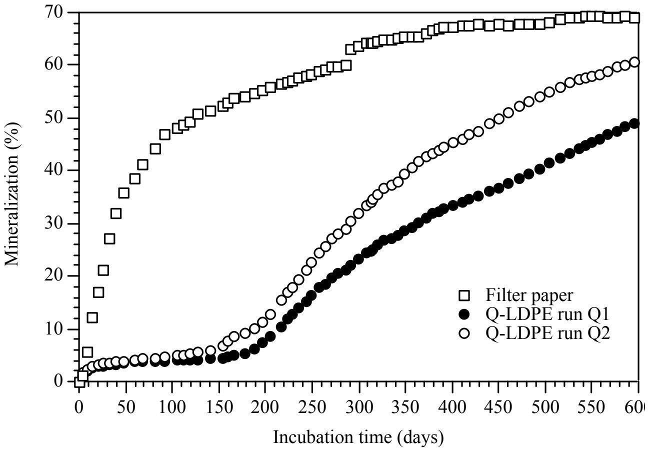

Figure 11: CO_2 evolution from oxidised TDPA™ PE (Q-LDPE) incubated in soil at ambient temperature

CONCLUSIONS

Biodegradation of polymers requires that the macromolecules be degraded initially by abiotic reactions. In the case of hydrocarbon polymers, such as PE, the first stage in such degradation is oxidation initiated by heat or UV light or mechanical stress. The oxidized fragments of the polymer chains are biodegraded in the second stage by the complex mixtures of microorganisms found in soil, in composting, or in landfill sites.

All of our data show that the TDPA® and Envirocare™ additive packages can accelerate the initial degradation of many hydrocarbon polymers, to the point where they become biodegradable, in timescales which are acceptable for many practical applications, ranging from packaging to landfill cover. Control of the rates of the two stages, in the case of various commercial PE's, is achieved through a balance of appropriate additives. In this way, end-use performance can be altered to fit specific markets without altering the normal degradation pathways and products.

Independent testing has shown that full, direct food contact is permitted for both degradable and compostable film products. The additive formulations can provide sensitivity to near-UV light as well as to heat. The essential feature of the additive packages is control of the lifetime of the material.
The major benefit for the user of degradable films is convenience. After use, the plastic film or thicker part does not need to be recollected, transported to a collection centre and disposed of by burial, landfill or incineration. A second important benefit is that TDPA® and Envirocare™ additives can be used with ‘commodity’ plastics, with standard processing equipment and processing conditions ,without affecting the mechanical or the optical properties of the plastic and with only minimal implications for recycling. These materials make a clear case for being considered as “clean-green polymers”

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