

CONTROLLED –LIFETIME ENVIRONMENTALLY DEGRADABLE PLASTICS BASED ON CONVENTIONAL POLYMERS

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Introduction

To be considered as environmentally degradable, a plastic product must satisfy at least two requirements. On outdoor exposure or soil burial it must lose its mechanical properties rapidly enough to “disappear” visually, and the mechanically degraded material must be susceptible enough to biological attack to ensure its complete conversion to biomass without release of toxic products.

Among the numerous applications for commodity thermoplastics, films for packaging and moulded plastic containers are very important. Polyethylene (PE) and polypropylene (PP) are commonly used in these areas owing to the array of useful properties for which they are noted. 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, which have a relatively short use-life (weeks, months), following which the articles are no longer needed and are discarded. At this point, the durability and persistence of man-made, macromolecular materials become disadvantages. There are a number of recognized real-life situations when biodegradability would be a very useful property, but polyolefins (and most other man-made polymers) are bioinert.

For microflora (fungi, bacteria and the like) to convert and assimilate the carbon in any substrate, a number of criteria must be met. The substrate must be water-wettable, and the constituent molecules must be sufficiently small that a very large number of their chain ends are accessible at the surface of the material. Hydrocarbon thermoplastics are bioinert 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 developing biodegradable packaging materials has been the use of intrinsically biodegradable polymers, typically aliphatic polyesters. These may be laboratory synthesised, synthesised from fermentation products, or produced directly by fermentation. An obvious example is poly(hydroxybutyrate), produced by bacterial fermentation. The aliphatic polyesters polylactic acid (PLA), polycaprolactone (PCL) and the polyhydroxyalkanoates hydrolyse under relatively mild conditions, to yield an array of small molecular fragments with acid or alcohol end groups. These are biodegradable, so that the bio-assimilation is a synergistic interaction between hydrolysis and biodegradation. Despite many years of research and development, these plastics have still to make significant impact in the marketplace. Indeed, most recent life-cycle analyses (Gerngross and Slater, 2000) suggest that the energy costs of producing most of the so-called “green” plastics will make them uncompetitive for many years to come.

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 PE and PP will degrade naturally, the timescale is too long for them to be considered an environmentally “friendly” materials 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.

We have developed additive packages which can be incorporated into conventional hydrocarbon polymers 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.

Polyolefin Oxidation and Biodegradation

The mechanisms of oxidative degradation of polymers, have been extensively studied and reviewed (See e.g. Scott, 1993). 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 into a chain reaction with oxygen and C-H bonds in the polymer, to produce a range of oxidation products. Although the primary products are hydroperoxides, their decomposition yields alkoxy radicals which are responsible for many secondary products. β -elimination of 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, they can tolerate only limited chain scission before becoming embrittled. It is well known that polyolefins that have undergone the normal processes characteristic of oxidative degradation, have hydrophilic surfaces and greatly reduced molar mass values. 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. (See e.g. Arnaud et al., 1994, Scott, 1997, 2000)

Cell enzymes, and particularly cytochrome P450 which is found on many bacteria, continue the 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 peroxy radical and hydrogen peroxide which is reduced by transition metal ions in the polymer to give the highly reactive hydroxyl radical. $\cdot OH$ initiates further peroxidation leading to continued biodegradation and ultimate bioassimilation to biomass and CO_2 so long as environmental oxygen and cell nutrients are available.

Thus, the bio-assimilation of degraded polyolefins is a synergistic oxo-biodegradation process. In that sense it is totally analogous to the two-stage, hydro-biodegradation, process by which linear polyesters are microbially assimilated.

EPI's Totally Degradable Plastic Additive Technology

EPI Environmental Products Inc. has developed a series of Totally Degradable Plastic Additive (TDPA™) formulations that, when compounded with conventional polymers at appropriate levels, control 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 speeded up 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 biodegradable.

TDPA™ formulations are typically supplied in masterbatch form, and incorporated into the final formulation at levels of a few percent. They comprise proprietary combinations of specific 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 TDPA™ formulations are processed on conventional equipment at normal speeds. The formulations are adaptable to common resins available from most well-known multinational suppliers.

Laboratory studies of Degradation

Polyolefins compounded with TDPA™ additives show rapid degradation in laboratory simulations of ageing. Laboratory experiments using FTIR spectroscopy, tensile testing and molecular weight measurement demonstrate rapid loss of mechanical strength and chain length and formation of oxidation products.

Typical results from IR spectroscopy are shown in Figure 1, which shows the carbonyl region of the spectrum for two samples degraded in an air oven for the same time under identical conditions, with and without additive. The extensive degradation of the additive-containing sample is clear.

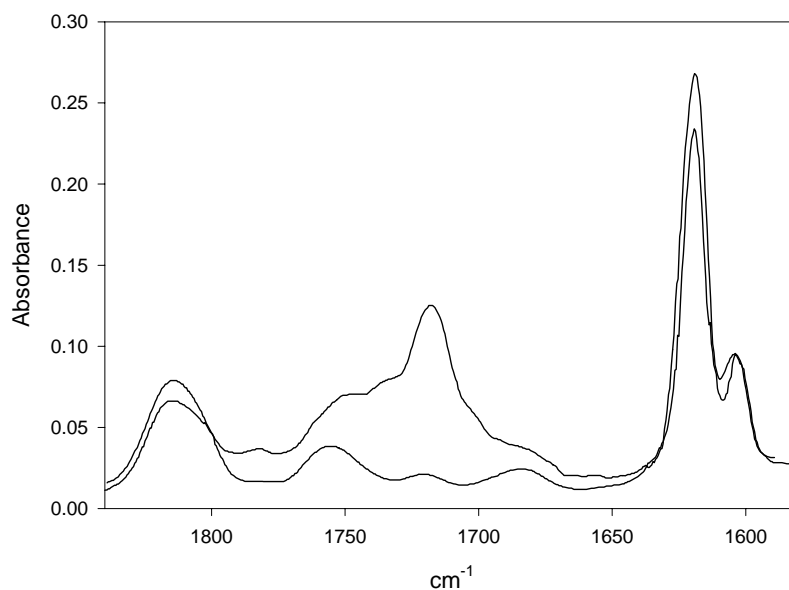


Figure 1: FTIR spectra of HIPS samples after air-oven ageing without (lower trace) and with (upper trace) TDPA™ additive

Degradation in laboratory conditions is also revealed by the data in Table 1, which shows the initial tensile properties of blown PP films produced with and without additive. With the additive present, the MFI increased to 40 after 90 days outdoor exposure. In an air oven at 71°C, the same material failed by embrittlement at 36 days. Without the additive, the material was still completely unaffected at the same times in the same conditions.

Table 1: Initial tensile properties and ageing data for blown PP film containing 3.0 wt% TDPA™ additive

Sample	MFI/ g 10min ⁻¹	Tensile strength/MPa	Extension to break/%	Time to failure	
				71°C Air Oven	Outdoors
0% TDPA™	12.0	48.5	800	No failure	No failure
3% TDPA™	14.6	47.3	904	90 days	36 days

Figure 2 shows the changes in tensile properties with time of QUV exposure for blown PP films. After 24 hours of exposure both the yield stress and the extension to break fall rapidly, indicating complete embrittlement; a similar polymer without additive showed complete stability in the same test.

It is important to emphasise that the TDPA™ additive package does not change the mechanism or products of the degradation of polymers. It simply accelerates the normal processes, leading to the same final products in shorter times.

Biodegradation and Composting

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 of defining biodegradability is fraught with hazards. Essentially all organic materials are

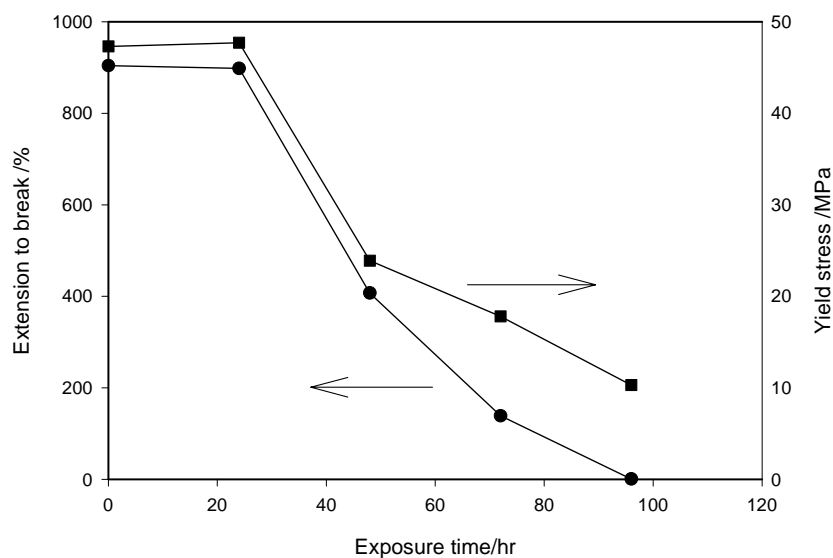


Figure 2: Modulus and extension to break for blown PP film containing 3.0 wt% TDPA™ additive subjected to QUV simulated weathering exposure

biodegradable in some timescale, though complete conversion to CO₂ and water (mineralisation) may take centuries. It is hard to see how, for example, the conditions in a landfill or composting operation could be simulated in small-scale laboratory conditions. Tests which require complete conversion of organic carbon to CO₂ 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 recognised 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 a contribution to the greenhouse phenomenon.

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 test 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 and litter.

Large-scale composting operations are well established in numerous countries, and serve as efficient means for producing useful material from what at present is largely garden and agricultural waste. Food wastes may also be used, and this would likely become much more common if inexpensive

"one-way " containers were available. Such containers would need to have the low cost and the serviceability of conventional PE bags but, in addition, would need to be compostable. 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."

Biodegradability of PEs modified by TDPA™ additives has been assessed by a variety of laboratory-scale and field-scale composting tests in the US and Canada. Most recently an extensive commercial-scale composting trial has been carried out in the municipal composting plant of Vienna Neustadt in Austria, under the direction of Dr B Raninger (University of Leoben).

This plant serves a population of about 100,000 people. In 1998 it treated about 10,000 tons of mixed household and green garden waste. Composting occurs in two stages: an in-vessel, forced aeration "tunnel" process, followed by an outdoor, open-pile windrow composting stage on a paved area with weekly watering and turning. The compost product is used mainly for landscaping and gardening.

The highly instrumented tunnels in the composting plant hold 90 m³ of waste. In the trials of our material the input to one of the tunnels contained just over 1 wt% of PE-LD bags (10,000 bags) which had been modified with the TDPA™ additive. The compost was examined after the main maturation period (2 weeks in the tunnel), after post-maturation (12 weeks outdoors) and after six months, all according to Austrian National Standard ON S 2200. Test protocols included mass loss, analysis for heavy metals and tests of seed germination and survival of daphnia and earthworms.

The results all show that PE films modified by our new additives are oxidatively biodegradable under composting conditions, yielding high-quality compost. No toxic effects could be detected on either seed germination or organism survival.

Samples of the compost containing biodegraded film were subjected to ecotoxicity testing. Tests included 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. All tests showed absolutely no toxic or harmful by-products. As an example, Table 2 shows germination rates and plant yields for cress and summer barley on standard compost and compost containing TDPA™ formulations. The final conclusion of this extensive test was that "EPI products using PE and TDPA™ technology meets the requirements to be classified as a degradable compostable plastic and the compost end product is fully acceptable as land fertiliser; EPIs products may be considered to degrade by successive abiotic and biological pathways in a manner that produces no harmful or toxic by-products".

Table 2: Germination Rates and Plant Yields on Regular and Modified Composts

Compost	Species	Germination /%	Plant yield/g
Blank	Cress	32.3	1.42
TDPA™	Cress	33.3	1.68
Blank	Barley	92	14.0
TDPA™	Barley	94	14.2

Some Applications of TDPA™ PE Films

(a) Plastics in Municipal Solid Waste

A landfill contains a complex mixture of many different materials in an environment which changes with the seasons and with the age of the site. However, from the work of Rathje and his students (Rathje and Murphy, 1992), we know that paper is the major component of landfills with plastic waste at about 10% by weight and increasing. We also know that everything in the landfill mixture persists for a very long time. Even readily biodegradable items such as food waste and cellulosic materials can last for several decades. It is not known how long conventional polyolefins will last because they have not yet undergone significant degradation in the oldest excavated landfills. The reasons for the reduced extent of chemical and microbial activity include relatively low temperatures in the winter and a lack of water and oxygen at the lower levels. On the longer term, even aerobic microorganisms are not very active under these conditions and most of the carbon that is metabolized is converted to methane by slow-acting anaerobic bacteria.

Plastic films, trash bags, containers and other articles discarded in municipal solid waste will end up in landfill sites, if not recycled or incinerated. When made of conventional polyolefins (as most are) they will last for many decades. If made using TDPA™ additive technology, household plastic waste, packaging, and industrial films will undergo the two-stage degradation process described above and return the hydrocarbon constituents to the biocycle much more rapidly. Plastic films for food wrap, bag and pouch applications represent situations where enhanced degradation (thermal followed by biodegradation) is an obvious advantage. It is important, of course, that the underlying technology have no impact on the food itself. In this context, it may be emphasized that the TDPA™ additive technology provides the required degradability while complying with the overall non-migration requirements of the FDA, and consequently EC Directive 90/128/EEC.

(b) Landfill Covers

It is required to cover the active face of a landfill at the end of each working day so as to reduce odour and visual impact, prevent scavenging, and prevent windblown litter. Commonly a daily cover of several inches of soil has been used, but this is costly and wasteful of space. A preferred alternative is a controlled-lifetime, environmentally degradable PE film, which is less expensive and obviously conserves space. Inexpensive attachments for conventional landfill-site equipment can be used to spread and secure suitably modified PE film. The film will remain intact for some time but will start to fail mechanically as molecular oxidation continues. Even in the lower levels of the site, as access by air and water becomes restricted, oxidative degradation will continue and bio-assimilation of the oxidized fragments will ensue.

Table 3 shows data which illustrate the characteristics of the proprietary product from EPI designated Enviro Cover (EC). It is concluded that more degradation occurred at the 6-foot level (1.8m) because of the greater exposure period but perhaps also because the heat generated from both chemical and microbial activity is retained more efficiently at the lower level.

Application to Polystyrene

It is obvious from the examples described above that our new additive technology can be modified to suit different environments and service conditions. This versatility is leading to other products in agricultural, marine and health care operations.

The TDPA™ technology is not restricted to PE and PP. In principle, since all hydrocarbon polymers degrade by similar mechanisms, the additive package can be adapted to any polymer system which does not contain biocides. As an example, we have investigated the use of the TDPA™ technology in injection moulded polystyrene cutlery, intended for one-cycle use.

Table 3 Degradation of Enviro-Cover Landfill cover film made from PE-LD with TDPA™ additive.

Sample	Tensile Strength/ MPa	Elongation at Break/ %	OD at 1715 cm ⁻¹
Control	16.9	550	0
⁺ Sample A [*]	9.6	446	0.02
⁺ Sample B ^{**}	5.6	128	0.08

⁺Film samples were buried in the Bailey Landfill, Chilliwack, BC, Canada for 98 days, from Dec. 14/95 to Mar. 21/96.

^{*}buried at the 3 foot level (0.9m)

^{**}buried at the 6 foot level (1.8m)

The additive was incorporated into the polymer at the 3 wt% level and the test cutlery exposed to air oven ageing at 71°C as usual. Figure 3 shows the changes in MFI with time of ageing. The rapid acceleration of molecular weight loss (MFI increase) at around 6-8 weeks of ageing of the treated material is in marked contrast to the decrease in MFI of the untreated material, which suggests some cross-linking. Visually, the treated cutlery is very markedly degraded and discoloured after 8 weeks of ageing, whereas the untreated material is visually unaltered. This is clearly visible even in a black and white image (Figure 4)

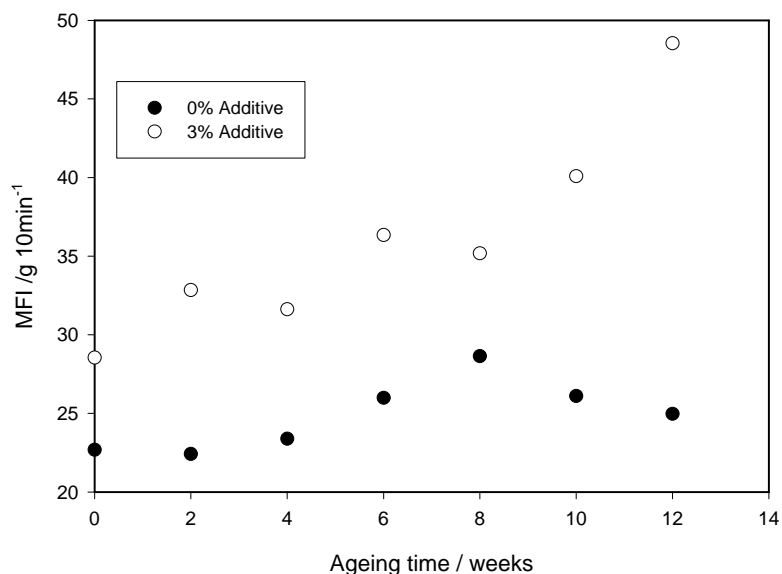


Figure 3 Melt flow index changes with time for polystyrene cutlery air oven aged at 71°C with and without TDPA™ additive.

Conclusions

Macromolecules can be degraded using abiotic processes such that the molecular fragments are biodegradable. In the case of aliphatic polyesters, for example, the first stage in this two-stage process is hydrolysis. The second stage is bioassimilation of the hydrolysis products. In the case of hydrocarbon polymers, such as PE, the first stage is oxidation initiated by heat or UV light or mechanical stress. The oxidized fragments of PE molecules are biodegraded in the second stage by the complex mixtures of microorganisms found in soil, in composting operations, or in landfill sites.

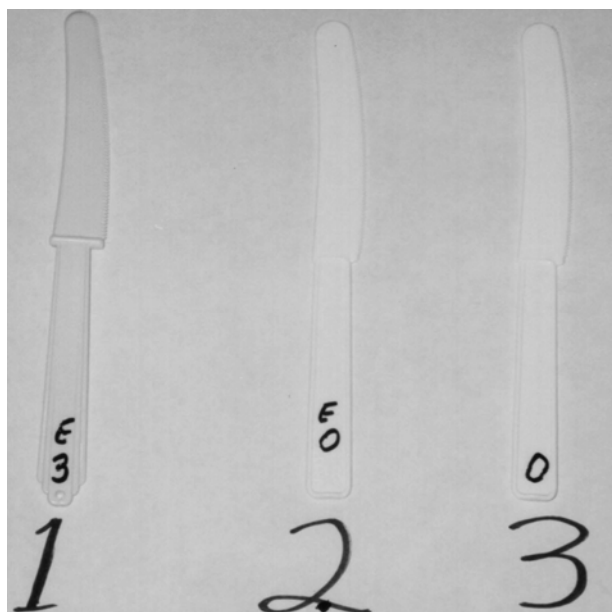


Figure 4: Injection moulded polystyrene cutlery before (3) heating and after heating at 71°C without (2) and with (1) TDPA™ additive

All of our data show that the TDPA™ 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 EPI TDPA™ film products. The additive formulations can provide, if required, sensitivity to near-UV light as well as to heat. The essential feature of the additive packages developed by EPI is control of the lifetime of the material.

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