



OXO-BIODEGRADABLE PLASTICS ASSOCIATION

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Response to "EuPC Answers to the EU Green Paper on plastic waste in the environment."

The Oxobiodegradable Plastics Association was surprised by the description of oxo-biodegradable technology in Section 2.21 of the EuPC (European Plastics Converters) "Answers to the EU Green Paper on plastic waste in the environment." Their now familiar description of the technology as *oxo-fragmentation* demonstrates both an ignorance of the complex degradation process and of the fact that oxo-biodegradable technology has been understood and accepted since the 1970's.

The European Normalisation Organisation (CEN) has defined the oxo-biodegradation process (in TR13531) as *degradation resulting from oxidative and cell-mediated phenomena, either simultaneously or successively*, but EuPC seem not to have appreciated the role of cell-mediated phenomena - ie consumption by micro-organisms.

It is difficult to understand how the negative attitude of the leadership of EuPC toward oxo-biodegradable plastic can serve their members, whose factories make products from plastic film. Oxo-bio can easily be used by them with their existing machinery and workforce, and it defends them against the often-heard criticism that they are making products which will lie or float around in the environment for decades if they escape into the open environment. Plastics converters in Europe and around the world are already using oxo-bio technology, and it is very much in the interests of EuPC members that they engage with the oxo-bio industry for their mutual benefit and the benefit of the environment.

The governments of the following countries carefully considered oxo-biodegradable technology as an option for dealing with the problem of plastic waste which escapes into the open environment. They then passed legislation which makes it mandatory to use the technology :- Pakistan, United Arab Emirates, Morocco, Mauritania, DR Congo, Mali, Togo, Cameroun, Yemen, Iran. Other countries will be following their example.

Plastics converters in Europe will not be able to export to those countries unless their products contain oxo-bio technology.

Respected Standards Institutions such as ASTM (ASTM 6954-04), BSi (BSi 8472) and AFNOR (N503-T54U and T51-808) have written standard test methodology to measure oxo-biodegradation and confirm that it does degrade and biodegrade and that it is non-toxic.

Independent testing of commercial samples of OXO'-TECHNOLOGY plastics has also routinely shown that these materials can be formulated to degrade rapidly to molecular-weight (Mw) values of well below 10,000. As an example, Fig. 1 shows the reduction of Mw for a commercial PE film aged according to the requirements of ASTM D6954.

The requirements of ASTM D6954 Tier 1 ($M_w < 5000$) and the UAE Standard 5009/2009 ($M_w < 5000$ in no more than 4 weeks) are achieved within 360 h of exposure, with the M_w falling from an initial value of 139,000 to 970 in 1392 hours. It is notable that the initial polydispersity index (M_w/M_n) fell from 8.6 to 2.3, consistent with completely random scission of the polymer chains.

A plastic is defined by ASTM D883 as "a material that contains as an essential ingredient one or more organic polymeric substances of large molecular weight...." Accordingly, no scientist would describe a material with a molecular weight as low as 5,000 as a fragment of plastic.

For EuPC to make unsubstantiated claims related to "risks of micro-plastics entering the environment, leaching of additives in the environment etc" when referring to oxo-biodegradability is irresponsible. The environment is much more likely to be polluted by fragments of the conventional plastic products produced by members of EuPC, which will lie or float around as fragmented pieces of plastic for decades before they finally degrade.

All polymers derive their mechanical properties, especially toughness, from the entanglement of their long molecular chains. Polymer chains long enough to confer useful mechanical properties are usually too large to be able to cross the cell walls of bacteria, algae, or fungi. All polymer biodegradation thus requires that there be some extra-cellular chemical process to cleave the chains and to release them from the entangled mass as components small enough to be transported into the microbial cell and metabolised. Also to add oxygen as organic functional groups and to shift from a non-polar to a polar behaviour.

There are two well-recognised biodegradation pathways for plastics, hydro-biodegradation, and oxo-biodegradation. The hydro- and oxo- prefixes are inserted to emphasise that biodegradation of a plastic always involves two stages, and both mechanisms are influenced by the environments to which the materials are exposed. There is nothing in nature to exclude oxidative scission as a precursor to biodegradation, and it is in fact the way nature disposes of both natural rubber latexes and the lignin fractions of wood, straw, and other plant matter.

Oxo v Hydro

Apart from the basic distinction between hydrolytic and oxidative cleavage, the main differences between Oxo' and hydro' technologies are;

- a) The lifetime of an Oxo' polymer, before biodegradation starts, can be regulated by varying the stabiliser/ pro-oxidant ratio. However, hydro' polymers begin to degrade as soon as they are exposed to moisture. Premature failure of hydro' plastics in moist conditions has been a common problem for the industry, especially in food packaging.
- b) Because of the induction-period required for oxidation to produce biodegradable materials, biodegradation of an Oxo' material is inevitably slower than that of a hydro' material. Although this excludes Oxo' plastics from applications requiring, or merely specifying, very rapid bio-assimilation, there are also many applications where the rapid and uncontrolled biodegradation of hydro' plastics is a problem.

In summary, the basic technology of an Oxo' material involves:

- a) An induction period during which oxidation catalysis by the pro-oxidant(s) is prevented by the stabilisation package. *During this period there is no change in the structure, properties, or performance of the polymer but the stabilisers are being consumed.*
- b) A rapid oxidation of the polymer during which chain-scission produces low molecular-weight materials, which are oxidised, hydrophilic, denser and polar.

- c) A period of bioassimilation of the oxidised materials, leading to mineralisation to CO₂ and biomass.

It is important to emphasise that these are overlapping processes. Once significant oxidation starts, it is faster in biotic than in abiotic environments, so that predictions from laboratory testing will tend to under-estimate the speed of degradation in natural environments. In nature the degradation and biodegradation act synergistically and enhance the overall process speed, as enzymes released by microbial activity will accelerate the oxidation process of the polymer.

The mechanism of oxidation has been the subject of innumerable studies since the pioneering work of Bolland and Gee in the 1940s on oxidation of rubbers. The peer-reviewed work of Ohtake's group in particular [1-4] has shown that "biodegradation of thin LDPE film in soil was unexpectedly fast because of the synergistic action of oxidative degradation on biological activity, which is probably due to the increasing hydrophilicity of the film surface."

Figure 1 also shows data for a commercial PP film. The requirement of Mw <5000 is achieved within 960 h of exposure, with the Mw falling from an initial value of 360,000 to 4290. The initial polydispersity index (Mw/Mn) fell from 7 to 2, again consistent with completely random scission of the polymer chains. Other independent studies are available and are appended as Annex 2 #3, and #4. All show the same behaviour; the initially high Mw of PE or PP is rapidly reduced to below 5000 by aerobic oxidation.

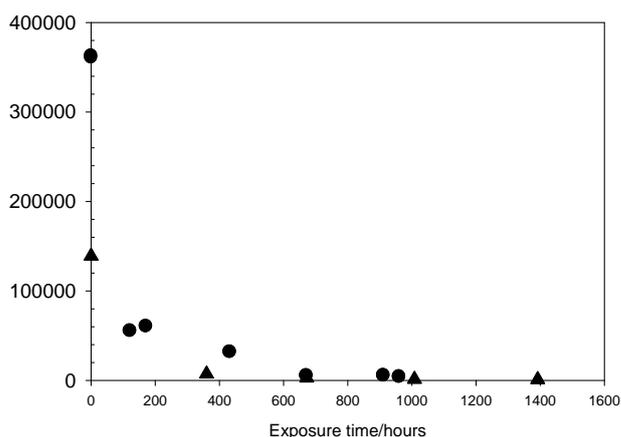


Fig. 1: Mw v time data for commercial Oxo' technology films aged as required by ASTM D6954 (▲ = polyethylene; ● = polypropylene)

It is important to recognise that the breakdown of a polyolefin to oxidation-induced embrittlement is not simply scission in the sense of breaking the film into pieces. It happens because the molecular-weight of the polymer is reduced to the point where it is no longer sufficiently entangled to be able to impart any strength. Because this molecular-weight reduction is caused by oxidative chain-scission it leads to materials which not only have low molecular-weights but are also significantly polar.

In their original study [7], Chiellini et al., studied oxidation of a commercial oxo' film, without any pre-treatment. The LDPE film was thermally degraded in air in an oven at 55 °C for 44 days. As shown in Fig. 2, the weight of the sample increased due to oxygen absorption, but, more significantly, at the end of oxidation the weight fraction soluble in acetone had risen to over 25%;

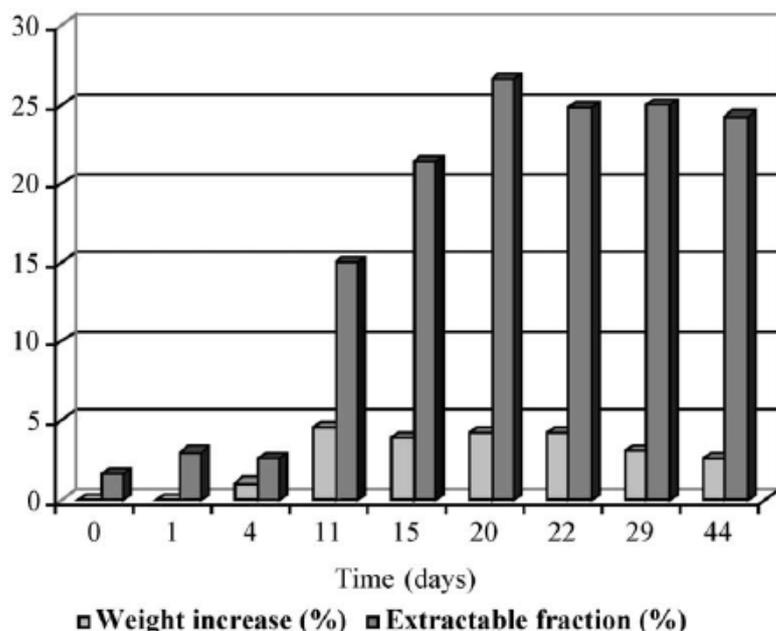


Fig. 2: Increase of dry weight and acetone extractable fraction of LDPE film with thermal degradation at 55°C [7].

Similar results were obtained by the same authors [8] in a study of thermal oxidation of several commercial oxo-technology films of LDPE at different temperatures (Table 1); acetone soluble fractions of up to ca. 30% were recorded.

Sample	CO _i ^a	Acetone extract		
		(%)	Mw ^b (kDa)	ID ^b
FCB-ZSK10	0.453	6.5	1.52	1.49
	0.534	7.7	1.47	1.46
	3.583	17.9	1.30	1.39
	6.816	27.1	0.92	1.32
FCB-ZSK15	0.212	5.9	1.58	1.46
	2.864	9.2	1.67	1.52
	5.193	23.8	1.27	1.43
	7.256	22.6	1.03	1.36
LDPE-DCP540	0.627	5.5	1.08	1.27
	2.243	11.3	1.49	1.41
	4.818	21.1	1.08	1.37
	5.441	27.7	0.89	1.33

^a Evaluated by FT-IR as $D_{B1640-1840}/D_{B1435}$.

^b Determined by HT-GPC.

Table 1: Relationship between carbonyl index (CO_i) and percentage extractable with acetone from original and thermally treated LDPE film [8].

PE is insoluble in acetone and these high weight fractions of extractable material, coupled with their low molecular weights and high carbonyl content as measured by FTIR, show that this material is no longer in any real sense PE; it is a highly oxidised and polar material.

These highly oxidised fractions are highly biodegradable. Fig. 3 shows mineralisation data obtained in soil burial experiments at 25 °C [7, 9]. They clearly show that these polar, oxidised fractions are as biodegradable as cellulose, the material used as a positive standard in biodegradation testing.

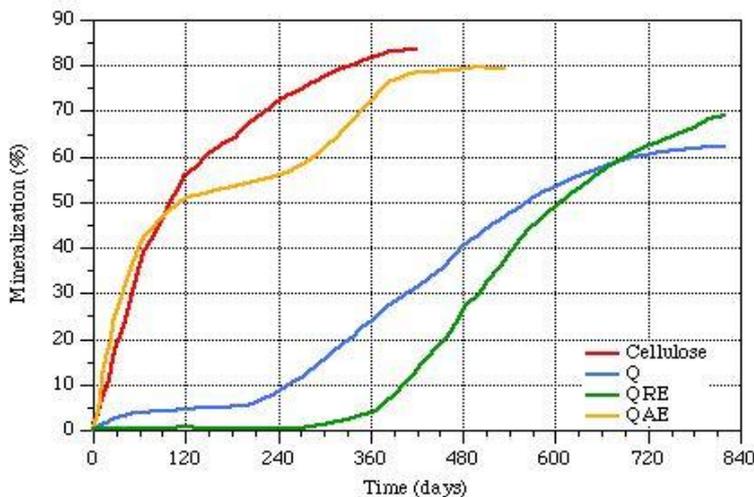


Fig. 3: Mineralisation in soil burial at 25 °C. QAE is the acetone extract from an oxidised LDPE film. [9]

Timescale of oxidative breakdown;-

There is robust peer-reviewed evidence that:

- a) Commercial oxo' technology films do degrade by oxidative chain scission to produce low molecular weight products.
- b) The products of oxidation are highly biodegradable.

The remaining issues are:

- a) What is the timescale of the oxidation in real-world applications? and;
- b) What is the evidence for completeness of biodegradation?

The paper by Jakubowicz et al., [10] used the Arrhenius approach to predict that their Mn-activated samples would have degraded to the point of biodegradability in between 2.5 and 4.5 years. It is important to recognise that the oxidative lifetime of any oxo' technology material depends upon the amounts of antioxidant and of pro-oxidant incorporated, and that lifetimes can be variable depending upon the formulation. This is a major strength of oxo' technology; it allows a sensible period of storage and useful life without degradation and it allows the material to be recycled with normal plastics during that period of time.

There are good reasons for believing that oxo' materials can be made to degrade in shorter times. In one recent paper [11], Ojeda et al studied degradation of a commercial HDPE/LLDPE blend containing a pro-oxidant additive and taken from the market as a supermarket bag. They showed that oxidation reduced the weight-average molecular weight from its initial value of 183,000 to 8300 after only 280 days of outdoor exposure.

Jakubowicz [12] recently presented data derived from testing of some commercial oxo' films using Mn-based pro-oxidant. As in previous work, they aged the samples thermally, in the dark at slightly elevated (40 to 75 °C) temperatures and used the Arrhenius equation to predict lifetimes to oxidative failure at 25 °C ranging from 65 to 330 days (Fig 4).

It should be noted that:

- a) This data was produced at SP laboratories in Sweden, a Government-accredited independent testing body with no connection to commercial producers of oxo' technology products.
- b) the samples used were commercial products, and
- c) the predictions of lifetime are in agreement with actual test data in soil exposure (discussed below).

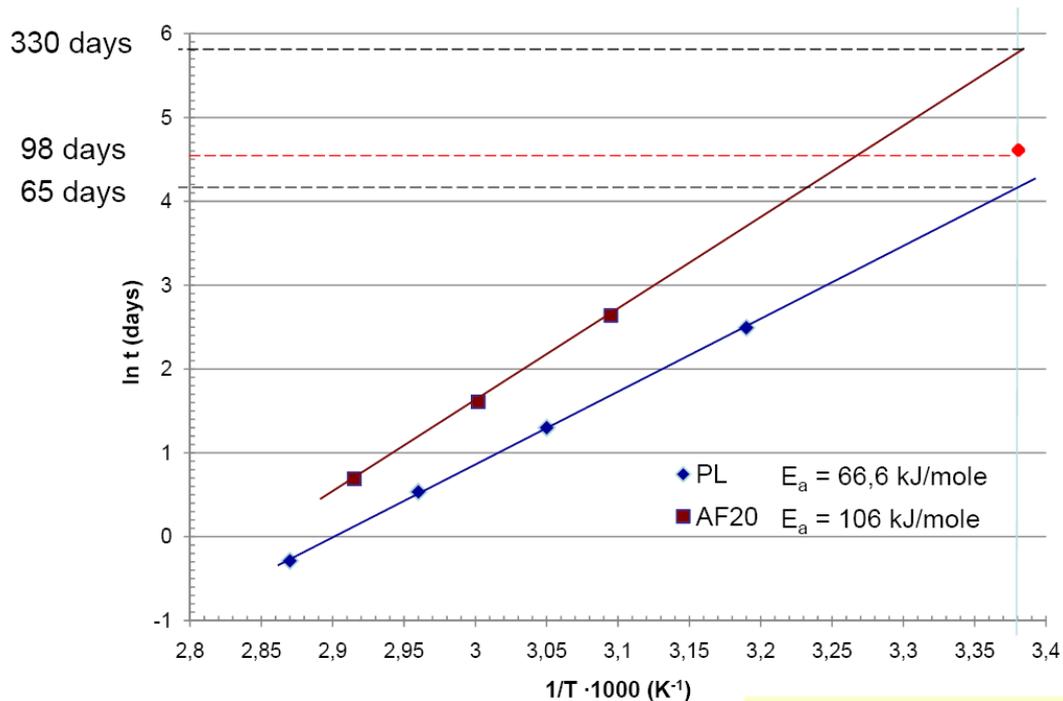


Fig. 4: Arrhenius plots for degradation of commercial oxo' technology films. Reproduced with permission from [12].

Corti et al. [6] showed that once a commercial mulch-film sample exposed to light began to oxidise, subsequent oxidation was significantly faster in a biotic than an abiotic environment at 23 °C. They suggest that abiotic oxidation of the polymer's carbon backbone produced metabolites which supported metabolic activities in fungal cells leading to further biotically-mediated polymer degradation. Thus, the combined impact of abiotic and biotic factors accelerated the oxidation/biodegradation of the films.

A similar study formed part of an evaluation of commercial materials, conducted by Chiellini's laboratory at the University of Pisa in Italy. FTIR measurements of oxidation in an oxidised oxo' film which had been incubated in the presence of an organism (*S. griseus*) capable of secreting oxidising enzymes showed that the material underwent significant oxidation as compared to the same film without exposure to the micro-organism.

These results clearly show that oxo' technology materials can be degraded by oxidation to the point of total embrittlement at ambient temperatures in periods of less than a year if formulated for that purpose.

Biodegradation and Composting

One false impression is that biodegradability and compostability are the same thing. This is far from true. The environment of an industrial composting facility is quite different from that to which oxo' polymers are expected to be exposed in the open environment for which they are designed. The temperatures, the moisture, and the likely microbiological activity are quite different.

EN 13432, ASTM D6400, and other composting standards were developed to place a very high barrier to the entry of any plastic into industrial composting and, as far as we are aware, no reputable manufacturer makes claims of compostability for oxo' plastics.

It is important to note the "compostable" plastics conforming to EN 13432 or ASTM D6400 cannot be made into compost. This is because those standards

require them to convert rapidly to CO₂ gas, which is emitted as a greenhouse gas to atmosphere, leaving nothing of any value for the soil.

The most likely disposal routes for oxo' plastics are recycling, landfill and soil surface exposure/burial (litter and Agricultural, horticultural and soil remediation applications), so that degradation in soil-contact is much more relevant.

Because of market requirements, commercial oxo' materials have been independently tested in several countries. For example, there is a report from the Chemical Industry Institute of Shihezi University, China, on the performance of a PE mulching film. The material was recovered from a field after one growing-season and tested according to ISO 14855:1999 in a controlled composting environment; it was shown to reach 77% conversion of carbon to CO₂ in 45 days. Another report is from the China National Centre for Quality Supervision and Testing of Plastics Products, on the testing of oxo-biodegradable polypropylene lunch boxes, again to ISO 14855:1999, after pre-oxidation in a controlled composting environment. The requirement was for 30% conversion of carbon to CO₂, hence the test was stopped when this was achieved. This material achieved 33% conversion in 126 days.

In the work of Chiellini et. al. on a commercial material, presented in Annex 2 #5, respirometric measurements of CO₂ production from an oxidised oxo' film which had been incubated in the presence of a micro-organism (*S. griseus*) showed that biodegradation was very much faster than that of the same film without exposure to the micro-organism, reaching 80% of the theoretical CO₂ yield in 130 days of soil exposure at 28 °C. This result was attributed to the demonstrable increase of oxidation by the biological attack by the micro-organisms once the oxidation had been initiated by thermal ageing.

Jakubowicz [13] has also shown that some oxo' plastics may degrade more slowly in active composting than in air. The published studies by Chiellini et. al. show *faster* bioassimilation of OXO'-TECHNOLOGY plastic in soil at 25 °C than in compost at 58 °C and the most recent work of Jakubowicz, reported below has confirmed this.

Studies by Jakubowicz et al in soil according to ISO 17556 support the results of Chiellini about faster bioassimilation in soil than in compost; when the same samples were tested in soil at 25 °C (Fig. 5), they had an induction time of around 300 days then achieved 80% mineralisation in a further 300 days. *The final mineralisation after 700 days was 91%.*

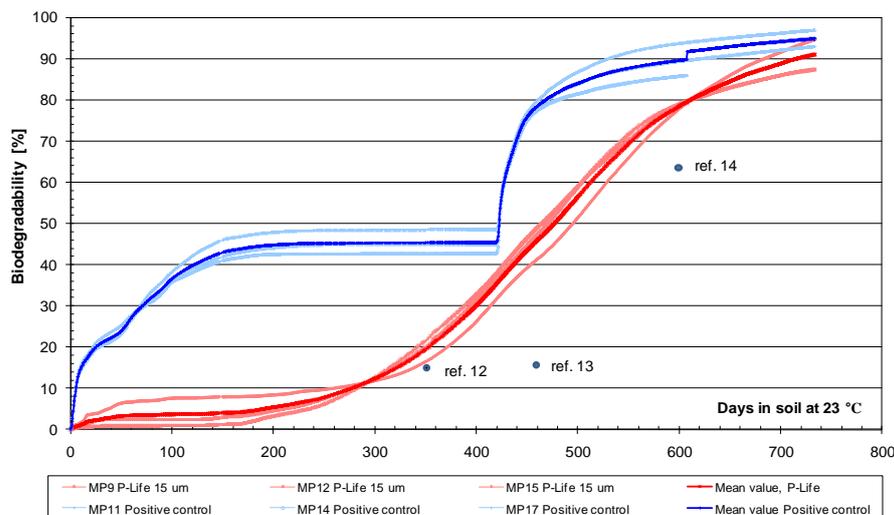


Fig. 5: Compost mineralisation of commercial oxo'technology films. Reproduced with permission from [12, 14].

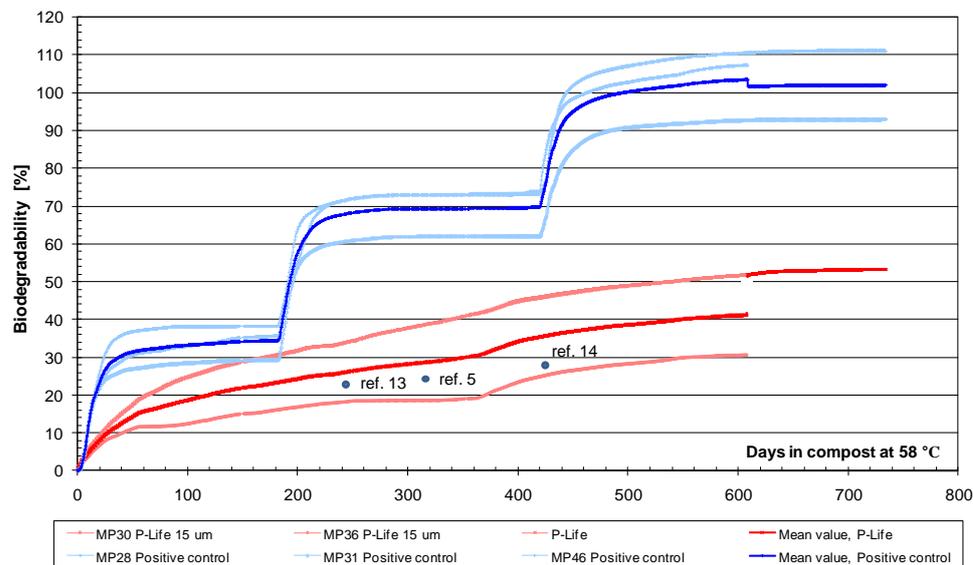


Fig. 6: Soil burial mineralisation of commercial oxo-technology films. Reproduced with permission from [12, 14].

A study of the bacterial and fungal populations of the soil and compost suggested that there were distinct differences which accounted for the ability of the soil microbes and fungi to metabolise the plastic more rapidly than in compost.

Given that these results were obtained by a wholly independent Government accredited Laboratory of the highest reputation, using commercially sourced samples, it is worth quoting from the conclusions in ref. [14]:

"After two years in the soil mineralization experiment, 91% biodegradability was achieved without reaching a plateau phase. This result has two important implications. The most important one is that it is possible to create LDPE based materials that will almost completely biodegrade in soil within two years. It also indicates that the risk of plastic fragments remaining in soil indefinitely is very low.

Recyclability

With regard to recycling, mentioned at para. 2.12 of the EuPC paper, it is well known that if oxo-biodegradable materials are collected for recycling during their useful life, they will not interfere with the process. See <http://www.biodeg.org/position-papers/recycling/?domain=biodeg.org> There is no need to keep them separate from normal plastics in the waste stream.

It is equally well established that bio-based "compostable" plastics can not be recycled with ordinary plastics and EuPc are correct that even a 2% contamination can affect the quality of the recycled plastic.

In the UK shopper bags produced in oxo-biodegradable material for Tesco and Co-Op were successfully recycled. The influence of anti-oxidants and stabilisers in polyolefin is a highly significant aspect of the processability and final performance of finished plastic products, and a full understanding of their relevance will inform an observer of the real-life performance of oxo-biodegradable materials in the recycling stream.

The length of the useful life of an oxo- plastic product is determined by the ratio of the concentrations of the antioxidants and of the pro-oxidants contained in the particular formulation, which can be modified so that the plastic product degrades according to whatever approximate timescale is required.

It is important to recognise exactly what is happening in an oxo'technology plastic in the early stages of its life. As in all plastics, the presence of traces of peroxides initiates radical reactions in the material and this is accelerated by the pro-oxidant catalyst in an oxo'technology material. The main effect of the antioxidants is to trap these radicals and prevent their attack on the polymer. *Until the antioxidants are consumed and oxidation of the polymer starts, there is no change in the polymer.*

Obviously if *any* plastic is to be recycled it must be collected and processed before it has become degraded. Oxo'technology products will normally have a useful life before embrittlement of at least 18 months, and if they have not been collected and recycled by then, they probably never will be.

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15. Some Publications by Professor Gerald Scott, DSc, FRSC, C.Chem, FIMMM, Professor Emeritus in Chemistry and Polymer Science of Aston University,

UK; Chairman of the Scientific Advisory Board of the Oxo-biodegradable Plastics Association; Chairman of the British Standards Institute Panel on Biodegradability of Plastics.

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