www.biodeg.org

Oxo-Biodegradable Plastics Association
A not-for-profit Association Limited by Guarantee.

EU registration no. 370641927438-79

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11th October 2019

Dear Sir,

We are giving evidence below in response to the Call for Evidence issued on 22nd July 2019 concerned with STANDARDS FOR BIO-BASED, BIODEGRADABLE, AND COMPOSTABLE PLASTICS. Please acknowledge receipt.

EXECUTIVE SUMMARY

- Oxo-biodegradable plastic is a type of biodegradable plastic completely different from bio-based and compostable plastics and should not be confused with them.
- Oxo-biodegradable plastic is not the same as oxo-degradable plastic, and should not be confused with it.
- Oxo-biodegradable plastic is designed to biodegrade if it gets into the open environment as litter. It is not designed for composting or landfill
- Ordinary plastic leaves fragments of plastic in the environment – oxo-biodegradable plastic does not.
- The only environmental conditions necessary for oxo-biodegradation are oxygen and bacteria – no special conditions are required.
- There is already a Standard (ASTM D6954) which has been widely used since 2004 for proving degradation, biodegradation, and non-toxicity of oxo-biodegradable plastics. There is no need for another standard.
- Oxo-biodegradable plastic should not be marketed as such unless it complies with ASTM D6954
- Oxo-biodegradable plastic is a British technology which has been in use for more than 20 years around the world, with no reports of environmental problems.
- Oxo-biodegradable plastic is intended to replace ordinary plastic for everyday items, at little or no extra cost.
- Oxo-biodegradable plastic is used for items for which recycling does not normally make economic or environmental sense, but it can be safely recycled without the need for separation.

DEFINITIONS

We are not directly concerned with bio-based or compostable plastics, though we will mention them where appropriate. We are concerned with "biodegradable plastic" but this is a term which causes confusion because it encompasses technologies which are completely different from each other and are not usefully conjoined under a single description. Going forward we take the view that government and other stakeholders should cease to use the term "biodegradable plastic" and should make it clear whether they mean oxo-biodegradable or hydro-biodegradable (eg compostable) plastic.

It is also essential to understand the difference between (a) OXO-degradable and (b) OXO-*bio*degradable plastic – (a) "Oxo-degradation" is defined by CEN (the European Standards authority) in TR15351 as "degradation identified as resulting from oxidative cleavage of macromolecules." This describes ordinary plastics, which abiotically degrade in the open environment, but do not become biodegradable except over a very long period of time.

By contrast, (b) "oxo-*bio*degradation is defined by CEN as "degradation resulting from oxidative and cell-mediated phenomena, either simultaneously or successively." These are plastics which become biodegradable much more quickly, as a result of oxidation accelerated by a catalyst.

INTRODUCTION

The Oxo-biodegradable Plastics Association (OPA) exists to provide information to encourage greater understanding of oxo-biodegradable plastic technology and how it can protect the environment for future generations. There are 1,602 members of the Association, who are manufacturers, distributors, importers, exporters and commercial end-users of oxo-biodegradable plastic products in 96 countries.

We will deal with the specific points made in the Call for Evidence, but it may be helpful if we first explain the context in which oxo-biodegradable plastic was invented and has been in commercial use for more than 20 years.

It is obvious to most people that plastic is immensely useful, and is the best way to prevent food wastage and sickness, by protecting our food from contamination and damage. It is much better than paper, cardboard or cloth, particularly when wet - but there is one fundamental problem – that if it gets into the open environment as litter it will create microplastics and will lie and float around for decades and perhaps for 100 years, before biodegrading.

In many countries, including the UK, measures have been adopted for reducing the amount of plastic in use and for redesigning and recycling plastic products. These are desirable aims and we support them, but it is unrealistic to think that these measures are going to prevent all plastic waste getting into the open environment, even in the developed world, for the foreseeable future.

The situation is alarming at global level, with 8 million tonnes ending up in the sea each year. This plastic will rapidly fragment into microplastics which can lie or float around for many decades. A substantial amount of plastic will continue to get into the open environment from which it cannot realistically be collected, and it is this fraction of plastic waste for which most of the world's governments and large businesses have no immediate answer.

That is the reason why there is so much opposition to plastic, almost amounting to plastiphobia, but it is **now possible to solve this problem by redesigning the plastic itself using oxo-biodegradable technology.**

The scientists who had invented plastic realised that the durability which they had worked so hard to provide would cause a problem if the plastic gets into the open environment as litter. They therefore looked for ways to make the molecular structure of the plastic dismantle automatically when it had served its purpose, and they created oxo-biodegradable plastic.

This is British innovation, led by Professor Gerald Scott of Aston University, who published "Polymers and the Environment" (ISBN 1-4020-0790-6) and very many scientific papers on this subject. We are attaching a pdf copy of three of his publications. Professor Scott was later appointed Chief Scientific Adviser to the OPA, and he has now died.

It is important to understand that oxo-biodegradable plastic is intended to REPLACE ordinary plastic with a material which performs just as well, and is not significantly more expensive. It must therefore be **compared with ordinary plastic, not with some ideal substance which does not exist**, and this is an important point made at Page 12 point 3.6(b) of the Call for Evidence. We all know that ordinary plastic will create microplastics with a dwell-time in the open environment of perhaps 100 years, and a judgment must be made whether a much shorter dwell-time is desirable.

The largest bakery in the western world, Grupo Bimbo of Mexico, ($US15.1bn revenues across 32 countries), which owns Sara Lee in the United States, has been successfully using oxo-biodegradable packaging for eleven years, and has now decided to expand its use for further products and in more countries.

The London Stock Exchange has introduced a new Green Economy classification and mark for listed companies. One of the OPA's British members, Symphony Environmental, meets the criteria and is included within the first cohort of companies to be recognised in this way. Symphony is the world's leading supplier of oxo-biodegradable plastic technology.

OXO-BIODEGRADABLE PLASTIC

This has been in use around the world for more than 20 years, and is now used in 96 countries. Oxo-biodegradable plastic products are made from ordinary polyethylene, polypropylene or polystyrene, but the manufacturer of the product adds a catalyst (which is not a heavy metal) to the polymer mix. This accelerates a change in the molecular structure if it becomes litter in the open environment, so that **it becomes biodegradable much more quickly than ordinary plastic**. Oxo-biodegradable plastic can be made by existing plastics factories at **little or no extra cost**, with no need to change their machinery or to create unemployment.

The only environmental conditions necessary for oxo-biodegradation are oxygen and bacteria, both of which are found everywhere in the open environment. Biodegradation in landfill is not necessary, and would generate methane.

We have seen the evidence sent to you on 8th October by Professor Emo Chiellini.

The confusion about oxo-biodegradable plastic is caused by people who do not understand the technology but cannot resist talking and writing about it. We have noticed that many of them do not know the difference between oxo-degradable, oxo-biodegradable, and bio-based plastics.

As a general point, we have found that reports and literature-reviews by researchers who are not experts in oxo-biodegradable technology show a lack of understanding of the mechanism by which oxo-biodegradable plastics acquire biodegradability, and the function of the stabilisation package. This leads to testing in conditions, and according to standards (e.g EN13432 or ASTM D6400), inappropriate for oxo-biodegradable plastics.

Queen Mary
University of London

A published study by Queen Mary University, London in August 2019 http://www.biodeg.org/wp-content/uploads/2019/08/qmu-press-release-15-8-19.pdf has confirmed that:

- Molecular-weight reduction is a critical factor in rate and extent of biodegradability
- The use of a prodegradant catalyst caused rapid molecular-weight reduction;
- The degraded polymer was then biodegraded by bacteria commonly found in soil and marine environments
- Oxo-Biodegradable plastic demonstrated up to 90 times more mineralisation that ordinary plastic
- There is similar biodegradation whether the polymer is degraded in the laboratory or under real-life conditions.

See also:

18 Jul 2018 Dussud et al 'Colonisation of Non-biodegradable and Biodegradable Plastics by Marine Organisms', published in 'Frontiers in Microbiology' Vol. 9 Article 1571 (peer-reviewed)

3 May 2018 Dr Ruth Rose, Letter to the European Chemicals Agency (attached)

23 Nov 2017 Arráez et al. Thermal and UV degradation of polypropylene with pro-oxidant. Abiotic characterisation', published in Journal of Applied Polymer Science DOI: 10.1002/APP.46088 (peer-reviewed)

23 May 2017 Eyheraguibel and 9 colleagues, Paper, 'Characterisation of oxidised oligomers from polyethylene films by mass spectrometry and NMR spectroscopy before and after biodegradation by a Rhodococcus rhodochrous strain, published in Chemosphere vol 184, page 366 (peer-reviewed).

Every day we read or hear opinions about oxo-biodegradable plastic which are incorrect, and unfortunately much of this misinformation is widely disseminated. In order to make sure that we had not ourselves misunderstood the science one of our members commissioned an in-depth review of the scientific evidence by a former judge of the High Court in England - http://www.biodeg.org/wp-content/uploads/2018/11/15-page-written-opinion.pdf

He has confirmed that our understanding is correct. We are able to supply you with further scientific evidence on request, to prove everything we say.

SPECIFIC POINTS IN THE CALL FOR EVIDENCE

Page 5 point (a) *"overall sustainability of bio-based and biodegradable plastic products, particularly when in comparison with those made from other materials."*

It is hard to see any real justification for seeking to replace ordinary or oxo-biodegradable polymers with bio-based polymers. Ordinary polymers are made from a by-product of oil-refining, but oil is extracted from the ground for petrol, diesel, and aviation fuels **and would be extracted in much the same quantity even if plastics did not exist.** Until the world no longer needs these fuels it makes sense to use the by-product, instead of using land and water resources and fossil-fuels to grow crops from which to make bio-based plastics.

A Life-cycle Assessment by Intertek in May 2012 for the UK government confirmed that oxo-biodegradable plastic had the best performance of all materials used for making carrier bag and bread bags - http://www.biodeg.org/life-cycle-assessments/life-cycle-assessments-2/

Designation: D6954 - 18

Standard Guide for
Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation[1]

Page 5 point (b) *"Existing relevant plastic degradation standards."* Oxo-biodegradable plastics are tested according to ASTM D6954 There are also comparable standards in the UK (BS8472) the UAE 5009-2009) Saudi Arabia (SASO-2879) France (T51-808) and Sweden (SPCR 141).

Page 5 point (c) *"to ensure that they fully biodegrade in a reasonable timeframe in specified environments."* Oxo-biodegradable plastics are not designed to biodegrade in any special environment. They are designed to biodegrade in the open environment almost anywhere in the world, and are tested in the laboratory, under conditions expected in the open environment, to prove 1. Degradability, 2. Biodegradability, and 3 Non-toxicity.

Page 8 Point 1.3 "*Biodegradable plastics can be broken down into water, biomass, and gasses such as carbon dioxide and methane. Biodegradability depends on environmental conditions such as temperature, humidity, microorganisms present, and oxygen."* Correct, but the only essential condition for the abiotic phase of oxo-biodegradation is oxygen. Sunlight and heat will accelerate the process, but are not essential.

Once the material has become biodegradable it requires only the activity of bacteria or fungi, which will normally require some moisture. This is the same for all biodegradable plastics.

Page 8 point 1.4 *"Compostable materials are a sub-set of biodegradable plastics that break down safely into water, biomass and gasses under composting conditions."* They do not themselves convert into compost, they emit CO_2 rapidly to atmosphere, and they have been found to contaminate the compost with fragments of plastic.

Page 8 point 1.6 *"This could prove useful in specific circumstances where it is hard to recover the material for recycling, or when that material could otherwise enter the recycling stream but cannot be recycled due to contamination*."

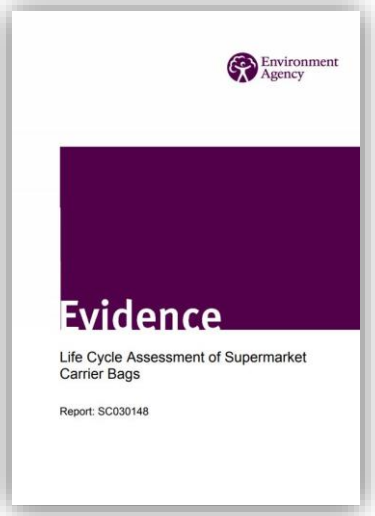
This is true of oxo-biodegradable plastic, and this is the reason for it. However, it is not true of other types of biodegradable plastic, because they have to be recovered and placed in a specific environment.

As to timescale, clearly oxo-biodegradable plastic products cannot be designed to degrade instantly, for they would then have no useful life, but as they are designed to degrade and biodegrade much more quickly than conventional **plastics there is a much shorter dwell-time for anything to accumulate in eco-systems**. In fact, if oxo-bio plastics had been brought into wider use even a few years ago the enormous ocean garbage patches would not have accumulated, and most of the plastic would have biodegraded and returned to nature.

The precise timescale depends on the formulation of the plastic product (some are designed to degrade faster than others) and the conditions in the environment where they are lying or floating. Sunlight and heat will accelerate the process but are not essential. They have a specific gravity less than 1, so they will normally float on the surface where oxygen, sunlight, and bacteria are abundant. They will nevertheless continue to become biodegradable if they sink or are covered. For this reason a broad indication only is given by the OPA as to timescale.

It is however **possible to say with certainty that at any given time and place in the open environment an oxo-bio plastic item will become biodegradable significantly more quickly than an ordinary plastic item**. That is the point. Do we want plastic which can lie or float around for 100 years, or plastic which will have been recycled back into nature in 2-3 years or less? Of course we don't want plastic in the sea at all, but that is not the reality for the foreseeable future.

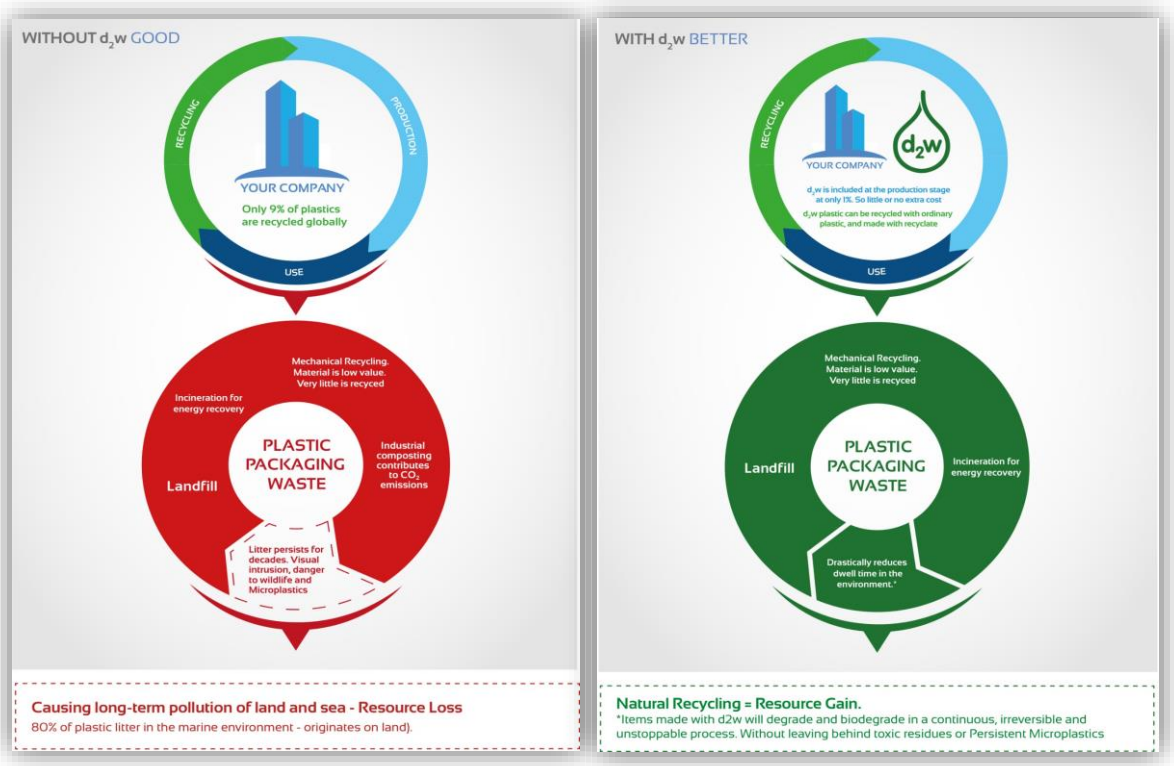
Page 8 point 1.7(a) "*Ensuring the UK has a manufacturing industry that can develop and thrive in a low carbon future economy, which could include replacing traditional fossil-based plastics with bio-based alternatives where recycled material is not available"*



As we have said, it is difficult to see any real justification for seeking to replace ordinary plastic with bio-based plastics. Compostable plastics will not be part of a low carbon future economy, because they are required by EN 13432 and ASTM D6400 to convert rapidly into CO2 gas, and they have greater global-warming potential than ordinary plastics. See

http://www.biodeg.org/wp-content/uploads/2018/11/uk-ea-publishes-lca-of-supermarket-carrier-bags-.pdf

Page 9 point (b) *"Circular economy: Ensuring any new materials entering the marketplace are compatible with a more circular economy in which we keep resources in use for as long as possible..."*



We support the principles of a circular economy but if a piece of plastic escapes from the circular economy and gets into the open environment, it is essential that it has been designed to become biodegradable much more quickly than ordinary plastic. Even if the plastic does not escape, it does not always make economic or environmental sense to send it for mechanical recycling. See below.

Page 9 point (c) *"reducing …. the environmental impact of that which is used, in both terrestrial and marine environments."* That is exactly what oxo-biodegradable plastic is designed to do.

Page 9 point (d) "*Citizen Clarity: Ensuring that the information provided to citizens is clear and helpful to enable people to make informed decisions about how they manage waste."* Agreed. As mentioned above under DEFINITIONS, it is essential for everyone (including government) to stop using misleading terminology such as "biodegradable plastic" and "oxo-degradable plastic."

An **oxo-biodegradable plastic should be marketed as such only if it is made with a masterbatch in respect of which its supplier can produce a test report as required by ASTM D6954** or a comparable standard for oxo-biodegradable plastic. Claims can therefore be verified, and **can be checked by the authorities using a hand-held detector.** There is no such detector available for hydro-biodegradable (e.g. compostable) plastic.

Citizens are being deceived by plastic being advertised as "compostable" and "biodegradable" because, as indicated above, it does not convert into compost and is not tested to biodegrade in the open environment. This practice should be stopped. The claim should be "will biodegrade in industrial composting but does not convert into compost. Cannot be recycled with ordinary plastic"

Page 9 point 1.8 "*a viable standard … for biodegradable plastic."* As indicated above there are so many types of biodegradable plastic that it is not possible to create one standard for all of them. We are concerned with oxo-biodegradable plastic, for which there are already viable standards (ASTM D6954 and comparable standards). These do NOT include EN13432 or ASTM D6400.

ASTM D 6954 has been in use since 2004, and has no less than six pass/fail criteria. We have seen the evidence sent to you on 8th October by Dr. Graham Swift, Vice-chairman of ASTM Technical Committee D20:96 and one of the authors of ASTM D6954.

Page 9 point 1.9 As to the Plymouth study**,** this was not a fair test of an oxo-biodegradable bag, (if the bag they tested was indeed oxo-biodegradable) because an oxo-biodegradable shopping bag contains stabilisers to give it a useful service life and which could have delayed the onset of abiotic degradation of the first bag for two years. Simply to say that it had not degraded after two years therefore gave a false impression. Also the researchers had folded it tightly so as to exclude most of the oxygen, and placed it in abnormal conditions - a dark environment below the surface of the water under a pontoon.

However, in another experiment the same researchers had exposed an oxo-biodegradable bag under normal conditions (i.e. with access to sunlight and oxygen) and found that it had degraded within 9 months. The researchers (who were not polymer scientists) did not measure the molecular weight of the degraded material so they were not able to say whether if had become biodegradable.

There is no doubt however that if the bags had been ordinary bags they would not have become biodegradable in the course of the experiment, and their fragments would lie or float around for decades – that is the alternative.

Page 10 Point 1.12. See Page 8 point 1.7(a) above

Page 11 Questions, Page 10 point 1.12 and Page 11 point 2.1 See Page 5 point (a) above

Page 12 point 3.2 the *products of biodegradation could be more harmful than the original piece of plastic itself, for example if they form microplastics which are much more difficult to remove from the open environment.*

Ordinary plastic will definitely form microplastics which are much more difficult to remove from the environment.

By contrast, Oxo-biodegradable plastic has now been in use for more than 20 years, and nobody would want to sell or buy it if it simply fragmented into tiny pieces, but this is not what it does. The process is well described by Professor Ignacy Jakubowicz as follows: "**The degradation process is not only a fragmentation, but is an entire change of the material from a high molecular weight polymer, to monomeric and oligomeric fragments, and from hydrocarbon molecules to oxygen-containing molecules which can be bioassimilated."** http://www.biodeg.org/Reply%20to%20Ellen%20MacArthur%20Foundation%20from%20Prof%20Ignacy%20Jakubowicz%20-%2021-8-17.pdf

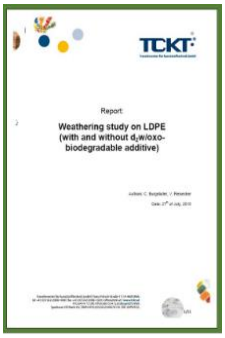
The products of degradation have to be tested for toxicity according to ASTM D6954 (paras. 6.9.5 – 6.9.10). If there is any toxicity they will not comply with ASTM D6954 and the product cannot be marketed as oxo-biodegradable.

Concerns also exist around the impact that biodegradable plastics could have on the move towards a circular economy and whether they impact adversely when entering.. recycling.

RECYCLING

Hydro-biodegradable (eg "compostable") plastic will certainly impact adversely when entering managed waste streams such as recycling, because it is completely incompatible with ordinary plastics.

Where plastic products are lightweight and contaminated with other materials, the energy and resources used in collecting, transporting, sorting, cleaning baling and reprocessing are more than those required for producing new plastics, and in such cases **recycling is not the most economic or environmentally sound option**. These are the very products for which Oxo-biodegradable technology is commonly used.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Report:

Weathering study on LDPE (with and without d_2w/oxo-biodegradable additive)


Roediger Agencies cc

ANALYTICAL LABORATORY

It is said that oxo-biodegradable plastic packaging cannot be detected by current technology at sufficient scale to be sorted out from conventional plastics. This is easily remedied by requiring the inclusion of a tracer in the oxo-bio plastic at manufacture which the equipment can recognise, but it is NOT necessary because **oxo-bio plastic can be safely recycled without separation**.

See the reports by specialist researchers in Austria and South Africa on our website at http://www.biodeg.org/recycling-and-waste/

In the last four years alone, enough masterbatch has been sold by one OPA member to make 600,000 tonnes of oxo-bio plastic products. We know that those products have been successfully recycled for the past 15 years by OPA members and their customers around the world, and in those 15 years we have heard **no reports of any difficulty encountered**.

It is said that oxo-biodegradable plastic packaging is - by its very design - not meant for long-term reusable applications. This is correct. It is meant for packaging which might become litter, and which is not normally reusable. This does not for example include PET bottles, which are worth collecting and recycling, and for which oxo-biodegradable technology is not suitable.

Even if the points made against oxo-biodegradable plastic in relation to recycling were valid, that is no reason to continue to use ordinary plastic, thousands of tons of which are getting into the oceans every day. These will undoubtedly create microplastics and will pollute the environment for many decades into the future. **Dealing with this long-term pollution is the most important issue of the day - not recovering low-value plastic materials by mechanical recycling.**

Page 12 point 3.3 *insufficient evidence to support any claim that the widespread uptake of biodegradable plastics would increase resource efficiency, reduce waste, or tackle plastic pollution.*

For the reasons mentioned above, there is no such evidence in relation to bio-based plastics. By contrast, for the reasons also mentioned above, oxo-biodegradable plastic would reduce waste and tackle plastic pollution, and has greater resource-efficiency than bio-based plastic.

Page 12 point 3.4 *many in the industry view marine environments as some of the most difficult in which to evaluate and achieve biodegradability, because of their varying levels of nutrients, oxygen, and temperature.*

This is true in relation to bio-based plastic, which is designed to biodegrade under controlled conditions in municipal composting. However, oxo-biodegradable plastic, as mentioned above at Page 9 point 1.8, does not require special environmental conditions, and will work anywhere provided that oxygen and bacteria are present. Oxygen is of course present in the sea.

There is also a terrestrial issue to consider, with challenges such as soil health and the effect that microplastic could have on terrestrial life (such as worms). ASTM D6954 provides eco-toxicity tests, including a specific test for worms (para. 6.9.10). The material should not be marketed as oxo-biodegradable if it does not pass.

Page 12 point 3.5 *At present our understanding is that there is an insufficient range of authorised toxicity tests within existing standards, in particular to ascertain the degree of toxicity of biodegrading plastics and the impact of microplastic particles in both terrestrial and marine environments. To some extent this is also true for conventional non-biodegradable plastics and, more generally, our understanding of the degradability of plastics in terrestrial and aquatic environments is limited.*

This is certainly true for conventional non-degradable plastics. However, for oxo-biodegradable plastics, ASTM D6954 does provide authorized toxicity tests in paras. 6.9.5 to 6.9.10. If the UK government considers that further or other tests are needed this can be discussed. As to microplastics see above under Page 12 point 3.2.

Page 12 points 3.6 (a) and (b)

(a) Fate and biodegradation of plastics: to improve understanding of the degradation of biodegradable plastics in the natural environment, and to clarify rates of decomposition to include a particular timescale for decomposition;

(b). Environmental impact: to improve understanding of the potential harm caused through the transport, accumulation, and degradation of biodegradable products and their fragments in various environments, including uncontrolled environments, as compared to harm caused by non-biodegradable plastics;

See above under Page 12 point 3.2, and Page 8 point 1.6

Page 13 point 3.6(c) *Impact on waste recycling and other forms of recovery: to improve understanding of any potential problems caused by biodegradable plastics within the recovery streams (including recycling). This should take into account potential solutions to these issues and comparison to the impacts non-biodegradable plastics have upon other recycling and recovery waste streams;*

See above under page 12 point 3.2.

Bio-based plastics cannot be recycled without separation. There are also concerns that plastics marketed as "compostable" are not as useful as claimed

http://www.biodeg.org/wp-content/uploads/2018/09/compostable-plastic-german-study-1.pdf

See also http://www.biodeg.org/wp-content/uploads/2018/09/bad-news-for-compostable-plastics-from-german-courts-3-10-14.pdf

See also https://www.plasticstoday.com/sustainability/k-2019-setting-record-straight-on-oxo-biodegradable-plastics/34870161661646/page/0/2

When compostable plastics biodegrade, the end result is the same as for oxo-biodegradable plastics, namely water, biomass, and CO_2. Compostable plastics would fail an ASTM D6954 test because they require the special conditions found in industrial composting, including moisture and a highly microbial environment.

Page 13 point 3.6(d) *to establish the basis for inclusion of a test result threshold for deciding that a plastic has fully biodegraded or will do so, and the potential inclusion of additional tests to ensure full biodegradation in the natural environment relative to the application for which it is designed.*

See ASTM D 6954 above

Page 15 point 4.1 and 4.2

"Compostable" plastic does not deal with the problem of plastic waste in the open environment from which it cannot realistically be collected. This is because it is tested according to EN 13432 or ASTM D6400 to biodegrade in a composting facility – not in the open environment. Moreover, it does not convert into compost of any value to the soil, because those standards require it to convert into CO_2 greenhouse gas within 180 days.

Oxo-biodegradable plastic is not marketed for composting, and would not be accepted by industrial composters, although it will biodegrade in industrial "in-vessel" composting. It is not marketed for composting because it does not emit CO_2 gas quickly enough to satisfy EN13432 or ASTM D6400.

Home composting of plastics is not viable. A householder cannot be expected to comply with the conditions specified in the relevant standard (or even to have a copy of the standard), and even in properly managed industrial composting there are concerns that the compost may be contaminated with plastic fragments. In any event why would a householder need an expensive plastic bag when he can take kitchen waste to his compost pile in a bucket?

Page 15 point 4.3

Compostable plastic cannot be recycled without separation, as it is completely incompatible with mechanical recycling with ordinary plastic. There are in fact 19 reasons why this type of plastic is not suitable for anything other than municipal composting.

See http://www.biodeg.org/wp-content/uploads/2019/04/opa-19-reasons-why.pdf

Page 16 point 5.1

Specification appropriate for biodegradability in the variable open environments found across the world.

Bio-based plastics are not suitable for biodegradation in the open environment, and should be restricted to municipal composting, as to which there are existing standards (EN13432, ASTM D6400 etc.)

With regard to oxo-biodegradable plastics, the Standards already mentioned which have been adopted in the USA, the UK, Saudi Arabia, the UAE, Sweden and France are suitable for their purpose. No standard for oxo-biodegradable plastic has been adopted in the EU, as the relevant committee of CEN is dominated by the bio-based plastics industry**. It is not necessary for every country or region to have a standard, as ASTM D6954 can be universally applied**. Copies are readily available from ASTM International.

As Dr. Swift says in his response to this Call for Evidence "Of course, conditions in the open environment are variable but there is no need for a standard for each of these conditions. Provided that oxygen is present, a plastic complying with ASTM D6954 will become biodegradable much more quickly than ordinary plastic, and that is its purpose. Oxygen is ubiquitous, and most of the plastic litter is found lying or floating around with abundant access to oxygen, but it is possible to imagine a piece of plastic in anaerobic conditions where abiotic degradation cannot proceed. However if this is in a landfill it does not matter, because the plastic has already been properly disposed of.

It is also possible for a piece of oxo-biodegradable plastic to find itself in anaerobic conditions outside a landfill but this would be very unusual and does not invalidate the general proposition. It is for example possible for plastic to be deprived of oxygen by being heavily bio-fouled in the ocean or buried in sediment, but this is unlikely to happen quickly enough to prevent sufficient exposure to oxygen for abiotic degradation. If it did, then that small proportion of the global burden of plastic litter would perform in the same way as ordinary plastic – no better and no worse."

Page 16 point 5.3 *many biodegradability standards require that any extrapolation from laboratory tests to the field is demonstrated with appropriate evidence in addition to that provided through the standard. For example, one testing guidance document (ASTM D6954) cautions that, "…the results of any laboratory exposure in this guide cannot be directly extrapolated to actual disposal environments; confirmation to real world exposure is ultimately required as with all ASTM International standards". However, biodegradability technical standards committees have not so far produced detailed guidance on how to utilise standardised biodegradability test methods in the context of the open environment.*

As Dr. Swift says in his response to this Call for Evidence "ASTM D6954 contains a standard caveat, recognising that laboratory environments are isolated, unlike the dynamic natural environment - in which degradation and therefore biodegradation is likely to proceed more quickly. However, ASTM D6954 has been devised by myself and other specialists working in the field over many years to provide practical guidance as to how the product is likely to perform in commercial use.

It has been my experience that results from laboratory testing are very likely to be reproduced in the real world. I can see no cause for concern that they would not, and have seen no evidence that they have not. In particular I do not consider that persistent plastic fragments and smaller, microplastics would be left behind which could have any harmful effect on the open environment, and in particular marine life."

Page 18 point 6.1 *proper labelling and communication of the right messages are essential aspects of informed consumer decision-making, and certification systems already exist for some types of biodegradable products. However, there can be uncertainty over compliance especially if it is by self-certification.*

6.2 Feedback from industry has suggested that items labelled as biodegradable do not always meet the relevant criteria, leading to confusion on the market. Standards, or more robust criteria lists, could better ensure items placed on the market really do biodegrade, if correctly complied with.

Confusion is caused by failure of commentators and governments to use the correct terminology, referred to under "DEFINITIONS" above.

SASO in Saudi Arabia, and ESMA in the UAE are public authorities which certify whether plastic products may be sold as oxo-biodegradable in their country.

The OPA certifies whether products may be marketed as oxo-biodegradable, and is willing to discuss a public certification programme in the UK.

Page 19, point 7.1 *Waste Management*

Many industrial composters will not accept plastic at all. Others will accept it only if it is labelled as complying with EN13432 or its provenance is known to them. There is no need therefore for oxo-biodegradable plastic to be labelled "not for composting."

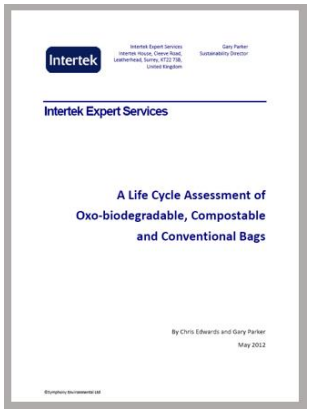
It is sometimes claimed that biodegradable plastics are likely to encourage littering, but this is rarely advanced as an objection to bio-based plastics. The Eunomia Report says, "rather than speculation, objective behavioural research is required to move this topic forward in a constructive manner."

In the view of the OPA, even if there were a label describing a product as oxo-biodegradable, it is unlikely that the people who cause litter will look for the label before deciding to throw a plastic item out of a car window. Further, even if it were true that biodegradability encourages littering, and supposing that there would be 10% more litter - is it preferable to have 110 plastic items in the environment which will degrade and biodegrade in a few years or even months, or 100 plastic items which will lie or float around for decades?

It is not acceptable to continue debating this speculative proposition any longer, while thousands of tonnes of conventional plastic are getting into the environment every day, which will accumulate and pollute the environment for decades into the future.

A Life-cycle Assessment by Intertek shows that when the litter metric is included OBP is actually **the best material for** making carrier bags.

See http://www.biodeg.org/wp-content/uploads/2018/11/intertek-final-report-15.5.121.pdf


Intertek

Intertek Expert Services

A Life Cycle Assessment of Oxo-biodegradable, Compostable and Conventional Bags

LEGISLATION

In some countries (notably the UAE, Saudi Arabia and Pakistan) the governments have realised that they cannot ban plastic because it is essential for the everyday lives of their people, but they also know that they cannot prevent large amounts of it getting into the environment as litter.

They have **therefore legislated to stop people using ordinary plastic and mandated the use of oxo-biodegradable plastic,** after doing extensive due-diligence themselves on oxo-biodegradable technology.

EUROPEAN UNION

By contrast, in Europe there has been much misinformation, confusion, and political/commercial opposition. The Single-use Plastics Directive (Recital 15) is intended to ban plastic that "does not properly biodegrade and thus contributes to microplastic pollution in the environment, is not compostable, negatively affects the recycling of conventional plastic and fails to deliver a proven environmental benefit." This applies to oxo-degradable plastic, but does not apply to oxo-biodegradable plastic, because there is solid scientific evidence that oxo-biodegradable plastic does properly biodegrade, does not contribute to microplastic pollution and does not negatively affect the recycling of conventional plastic.

There is a well-established procedure in the EU for deciding whether substances should be restricted or banned. This was negotiated with all stakeholders and is set out in Arts. 68-73 of the REACH Regulation 1907 of 2006. The EU Commission's report of January 2018 did not recommend a ban – it recommended that the matter be referred to the European Chemicals Agency (ECHA), and the Commission's proposal to the EU Parliament did not include a ban either.

In 2018 the EU Commission acted under Article 69 to request ECHA to study "oxo-degradable" plastics because the Commission thought that they created microplastics, but on 30th October (ten months into the study) **ECHA advised that they were not convinced that microplastics are formed** by oxo-biodegradable plastics.

If, and only if, ECHA had recommended a restriction, it would have had to be considered by two committees under Articles 70 and 71, and there would have had to be a public consultation, before any restriction could be implemented. **None of this has been done, and we are advised that any ban would therefore be unconstitutional and unenforceable**.

IN CONCLUSION, we would say that a proven technology is now available to upgrade plastic at very low cost so that it will not lie or float around for decades and be a problem for future generations. Countries in the Middle East and Asia have already legislated to make this technology compulsory for everyday plastic products, and we see no reason why the UK government should not do the same.

We are conscious that although our evidence extends to 15 pages there will inevitably be a number of issues which the UK government may wish to explore further. We would welcome a dialogue.

Yours sincerely,

Michael Stephen

MICHAEL STEPHEN
Chairman

ELSEVIER

Polymer Degradation and Stability 68 (2000) 1–7

Polymer Degradation and Stability

Invited review

'Green' polymers☆

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Received 7 October 1999; accepted 12 October 1999

Abstract

The utilisation of waste polymers by mechanical recycling and incineration have ecological limitations. Consequently, degradable polymers are gaining acceptance in biological recycling in areas of agricultural technology and packaging where the waste product is located in a microbially active environment. The ecological benefits of the synthetic polymers, particularly the polyolefins, are compared with hydro-biodegradable polymers made from renewable resources with emphasis on energy utilisation, environmental pollution and land utilisation. It is concluded that polymers that degrade by peroxidation followed by bioassimilation of the oxidation products (oxo-biodegradable polymers) are in general more environmentally acceptable ('green') than the the biologically produced hydro-biodegradable polymers.

Keywords: 'Green' polymers; Polyolefins; Oxo-biodegradable polymers; Hydro-biodegradable polymers; Photo-biodegradable polymers; Biologlcal recycling; Composting

1. Environmental impact of the synthetic polymers

The synthetic polymer industry has brought great benefits to modern society. For example in the packaging and distribution of foodstuffs and other perishable commodities the commercial thermoplastic polymers are hydrophobic and biologically inert and this has made them essential to modern retailing [1].

Similarly in agriculture, plastics have largely replaced glass in greenhouses and cloches and they have gained a unique position in the growing of soft fruits and vegetables over very thin polymers films (mulching films) [2]. The major group of polymers used in both packaging and in agriculture are the polyolefins which, due to their resistance to peroxidation, water and microorganisms, are durable during use.

In the 1970s, it became evident that the very technical advantages which made polymers so useful were disadvantages when polymer-based products were discarded at the end of their useful life and in particularly when they appeared as litter in the environment. The effects of some items of plastics packaging was found to be very damaging to wild-life [3] and this led to calls from the 'green' movement to return to biologically based (renewable) polymers. The popular view is epitomised in the following statement from Greenpeace [4]:

> Materials made from naturally occurring or biologically produced polymers are the only truly biodegradable 'plastics' available. Since living things construct these materials, living things can metabolize them.

In fact, this is a misunderstanding since there is no intrinsic difference between the biodegradability of bio-based polymers and synthetic polymers. For example, natural rubber [*cis*-poly(isoprene)], as it come from the rubber tree, is bioassimilated into the environment initially by peroxidation followed subsequently by biodegradatation of the low molar mass oxidation products (laevulinic acid, acetic acid, formic acid, etc.). Synthetic *cis*-poly(isoprene), manufactured from petrochemical feed-stocks, behaves in exactly the same way under the same conditions. However, both natural and synthetic *cis*-poly(isoprene) become highly resistant to biodegradation when made into industrial products (e.g. tyres). This has nothing to do with the inherent biodegradability of the *cis*-polyisoprene molecule. It is a

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☆ Adapted from a lecture given at the UNIDO International Workshop on 'Polymeric Materials and the Environment' at Doha, 21–25 March 1999.

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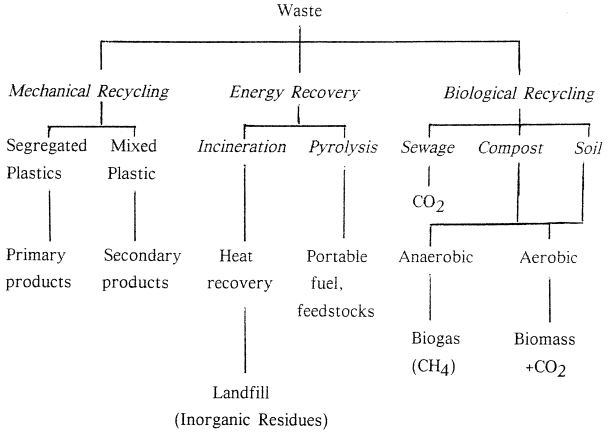
PII: S0141-3910(99)00182-2

direct consequence of the presence of highly effective antioxidants added during manufacture [5]. It has recently been shown [6,7] that polyethylene films, from which a small amount of antioxidant (BHT) had been removed, bioerode rapidly in the presence of bacteria whereas under, the same conditions, but before removal of the antioxidant, they were completely inert to micro-organisms. Significantly, natural polymers are not always bioassimilated more rapidly than petrochemical-based synthetic polymers. Felled sequoia trees survive in the biological environment for hundreds of years due to the presence of indigenous tannins which are both anti-oxidant and biostats [1,8]. Few if any synthetic polymers could survive in the environment for this length of time.

In practice, a relatively small weight proportion of polymeric materials ends up as litter. In most developed societies domestic organic waste, including plastics packaging, is disposed of in sanitary landfill or by incineration. However, burying waste is no longer an ecologically acceptable way of disposing of consumer wastes. Biological materials generate methane under anaerobic conditions and this is a much more effective 'greenhouse' gas than carbon dioxide. Methane has also been implicated in explosions in houses built on old landfill sites. Scheme 1 outlines the preferred alternative waste management procedures to replace landfill and it is predicted that increases in landfill levies coupled with the logistical costs of transporting urban wastes to rural sites will lead to the phasing out of this disposal option by the year 2015. Municipal waste management plans are increasingly reflecting this trend [1,9].

Of the alternative waste management options outlined in Scheme 1, incineration with energy recovery is at first sight an ecologically acceptable way of utilising carbon-based polymer wastes due to their high calorific value. However, there is a widespread distrust of incineration by the general public due to the possibility of toxic emissions from some polymers, particularly PVC which may produce dioxins during combustion. On the other hand, waste plastics are increasingly regarded as resources to be re-used. Mechanical recycling of individual polymers results in the reformation of similar but generally down-graded products. Mixed plastics by contrast are normally unsuitable for secondary applications. However, all plastics can be pyrolysed to give fuels, petrochemical feed-stocks and in selected cases, monomers [1]. Because of the growing importance of municipal composting, there is increasing interest in polymers that can be biologically recycled to biomass. As will be seen below, biologically recyclable polymers may be based either on renewable resources or on petrochemicals.



Scheme 1. Polymer waste management options [1].

2. Mechanical recycling

Experience in the reprocessing of industrial wastes in the traditional materials industries suggested to polymer technologists in the 1970s that similar procedures might be used to recover materials suitable for second use from polymer wastes. However, this proposal overlooked the fact that industrial polymers are organic materials and whereas glass and metals can be recycled to products with properties essentially similar to the primary materials, this is not so with polymers. In particular, each time polymers are reprocessed there is a loss in physical and mechanical properties due to per-oxidation. Furthermore, the re-processing operation itself uses oil-based energy. Table 1 shows that almost one third of the energy used in the manufacture of polyethylene is vested in the processing operation.

When reprocessing energy is added to the energy expended in transportation and cleansing the waste and in the additives used to provide a serviceable product, the ecological benefits of recycling is frequently lost and one or more of the alternative recycling processes outlined in Scheme 1 may be preferable. In spite of this caveat, some items of clean plastics may be with care recovered from the waste stream in bulk (e.g. industrial shrink-wrap, battery cases, crates and car bumpers) and blended into the primary application in a 'closed-loop' with clear ecological gain in terms of energy utilisation [1,10]. The situation is very different in the case of

Table 1
Energy balance in the manufacture and incineration of polyethylene (adapted from Ref. [14])

Energy utilised during manufacture	%
Crude oil to naphtha	9
Naphtha to ethylene	21
Ethylene to polyethylene	10
Polyethylene to finished product	17
Total energy used	57
Energy produced by incineration of the product	43

domestic packaging wastes. Materials recycling of household waste plastics is particularly difficult when they are contaminated with biological residues or, as is usually the case, when they are a mixture of different kinds of plastics [10]. A great deal of well intended entrepreneurial effort has gone into the development of special processing equipment to convert mixed plastics wastes to wood or concrete substitutes in the manufacture of fence posts, benches, boat docks, etc. [1], but there are serious doubts about the ecological benefits of doing this. For example in a recent study of recycling of mixed packaging waste, it has been shown that, to compete with conventional materials such as wood and concrete, the recycled products would not only have to perform as well as traditional materials but they would also have to last 3.3 times as long as the materials they replace [11]. Although at first sight mechanical recycling of consumer wastes appears to be a 'green' operation, practical experience has shown that reprocessing of mixed contaminated plastics produces polymer polyblends that are inferior mechanically and lacking in durability compared with those produced from virgin polymers [10,12,13]. Some limited success has been achieved with mixed plastics wastes in the manufacture of plastics-based underground chambers by increasing wall dimensions to match the load-bearing strength of concrete [1]. In this application, there is no significant long term deterioration due to exposure to the weather but this procedure could never utilise more than a small fraction of the mixed polymer wastes available. Considerable academic interest has centred round the use of 'compatibilizers' (more correctly, solid phase dispersants [10]) to upgrade the mechanical performance of mixed plastics polyblends [12,13] but in general this is an expensive and energy-intensive procedure which cannot be justified for domestic mixed plastics wastes.

3. Waste to energy

Energy generation by incineration of plastics waste is in principle a viable use for recovered waste polymers since hydrocarbon polymers replace fossil fuels and thus reduce the CO_2 burden on the environment. The calorific value of polyethylene is similar to that of fuel oil (Table 2) and the thermal energy produced by incineration of polyethylene is of the same order as that used in its manufacture (Table 1).

Incineration is the preferred energy recovery option of local authorities because they can gain financially by selling waste plastics as fuel [1]. However, in most developed countries public distrust of incineration at present limits the potential of waste-to-energy technologies. However, it should be noted that hydrocarbon polymers can produce only carbon dioxide and water on incineration and are consequently 'clean' fuels. At present, the most ecologically acceptable waste-to-energy process for waste polyolefins is incineration in furnaces and cement kilns [11].

Table 2
Calorific values of plastics compared with conventional fuels [1]

Fuel	Calorific value (MJ/kg)
Methane	53
Gasoline	46
Fuel oil	43
Coal	30
Polyethylene	~43
Mixed plastics	30–40
Municipal solid waste	~10

An alternative to direct incineration is to convert polymer wastes by pyrolysis or by hydrogenation to low molecular weight hydrocarbons for use either as portable fuels or as polymer feedstocks [1]. This is a highly specialised fluid-bed operation which is not appropriate for municipal waste disposal. It is the preferred solution of the polymer manufacturers since the hydrocarbons produced can be fed directly into their petrochemical operations. Doubtless, feedstock recovery from waste plastics is potentially important but energy costs, including waste transport, will play a major role in determining the viability of such plants.

4. Biological recycling

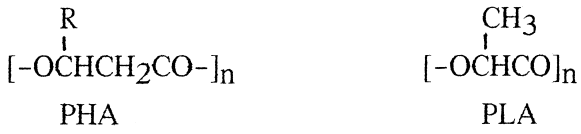
Nature's waste is returned to the natural carbon cycle by biodegradation. The primary product is biomass which acts as a seed-bed for new growth [8].

Biomass formation is also beneficial to the environment since it 'ties up' the carbon for a more extended period compared with incineration. The importance of making use of this natural process by controlled composting of organic wastes has been recognised by waste disposal authorities and a combination of mechanical recycling, energy recovery by incineration and composting will be the preferred alternatives to landfill by the second decade of the new millennium [15].

If man-made polymers are to be incorporated into this system then they must be ultimately biodegradable in compost and as litter. The present generation of commodity packaging polymers are not biodegradable within a realistic time scale due to the presence of antioxidants and this has led to intensive research both in industry and in universities to develop polymeric materials that conform to user requirements but are also returned to the biological cycle after use. Polymers must remain stable during manufacture and use but break down rapidly after discard [17–22] with conversion to biomass in an acceptable time [7,21]. The time to ultimate mineralisation of polymers in compost or as litter

is much less important than the time taken to fragment to small particles which can subsequently biodegrade over months or years [7,21,22] (see Fig. 1).

The biodegradation of polymers occurs by two quite distinct mechanisms depending on the nature of the polymer and the environment [1]. The first is abiotic or biotic hydrolysis followed by bioassimilation (hydro-biodegradation) and is the primary process involved in the biodegradation of the hetero-chain polymers such as cellulose, starch and the aliphatic polyesters of which poly(lactic acid) (PLA) and poly(3-hydroxyalkanoates) (PHA) are typical [1,23]. Normally, peroxidation plays a secondary role in these polymers but it has recently been shown that photooxidation can accelerate hydro-biodegradation [24]. Hydro-biodegradable polymers are suitable for cosmetic and personal hygiene products which normally end up in sewage (Fig. 1). They are not very suitable for agricultural films or packaging films (see below).



The second mechanism is peroxidation followed by bioassimilation of low molar mass products (oxo-biodegradation) and it applies particularly to the carbon-chain polymers. Abiotic peroxidation and hence biodegradation can be controlled accurately by the use of appropriate antioxidants [5,7,17,18,21,23]. The mechanical properties can be retained for months or even years without fragmentation in the outdoor environment but this protection is 'inverted' under the influence some component(s) of the environment (e.g. light and/or heat) with the formation of pro-oxidants [13,16,20,21]. Bioassimilation begins as soon as low molar mass oxidation products are formed [15,16,20,21]. Since this is much faster than the peroxidation process, the latter is the rate-controlling step in the overall biodegradation process.

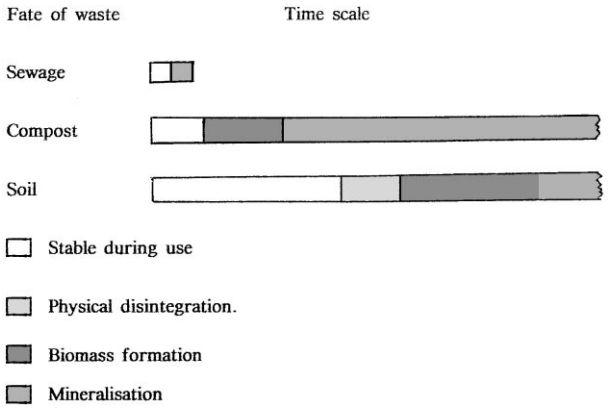


Fig. 1. Relative time-scale for polymer biodegradation in different environments.

At present, only about 25% of plastics waste is recovered for the recycling processes discussed above and in Europe about 65% of this is incinerated, the remainder being recycled to secondary products or to feedstocks [1]. Thus, 75% goes to landfill or ends up as litter. Biological recycling of polymers must then be considered as an alternative to the more traditional recycling procedures and this has stimulated chemists over the past 30 years to modify existing polymers as described above or to synthesise new polymers that can be returned to the biological cycle after use. This is particularly important for agricultural and horticultural plastics since collection for the alternative recycling procedures is both energetically and economically unfavourable.

5. Applications of biodegradable polymers

Two different applications have emerged over the past two decades for degradable polymers. The first is where biodegradability is part of the function of the product. Examples of this are temporary sutures in the body or in controlled release of drugs where cost is relatively unimportant. Similarly in agriculture, very thin films of photo-biodegradable polyethylene are used to ensure earlier cropping and to reduce weed formation [1,2]. By increasing soil temperature they also increase crop yields and ensure earlier harvest. A major ecological benefit of mulching films is the reduction of irrigation water and fertiliser utilisation [25]. No residues must persist in the soil in subsequent seasons to make the land less productive by interfering with root growth. Substantial economic benefits accrue to the farmer from the use of biodegradable polymers which more than justifies any increase in materials expenditure (Table 3).

A similar use of photo-biodegradable polyethylene films is to sterilise land by increasing soil temperature for some weeks before planting. This results in the removal of pathogenic bacteria without the use of methylene dibromide which is to be phased out by the year 2010 because of its ozone depleting effect in the environment [21]. A different ecological benefit is being

Table 3
Ratio of increased income to cost of mulching film [1]

Crop	Increased income/cost
Melons	13.0
Vegetables	5.0
Peanuts	3.9
Sugar cane	3.6
Cotton	3.0
Maize	2.5

achieved in Japan by the encapsulation of fertilisers in oxo-biodegradable plastics [26] which allows controlled release over a longer times scale, resulting in increased fertiliser efficiency and reduced eutrophication of rivers and lakes.

The second application of biodegradable polymers is in packaging. Retail outlets frequently claim that their packaging is 'environmentally friendly' because it can be 'recycled'. However, unless facilities are available to reprocess polymers, the claim is meaningless. Aerobic composting (oxo-biodegradation) is now emerging as a more convenient alternative means of adding value to recovered packaging wastes [9]. The polyolefins have a particular advantage in compost since, unlike the hydro-biodegradable polymers, once they have fragmented they mineralise slowly and increase the fertiliser value of the compost. Oxo-biodegradation also has important potential in the bioassimilation of obtrusive plastics packaging litter in the countryside and on the seashore. The former is primarily in the form of feed packaging, hay and silage stretchwrap packaging and baler twines [1]. Sea-borne plastics litter consists mainly of fishing nets, ropes and fishing crates together with packaging discarded from ships [3]. It seems inevitable then that environmentally biodegradable commodity plastics will have an increasing role in the management of waste and litter in the future.

6. Biodegradable polymers derived from renewable resources

We have seen that polymers based on biological resources are perceived as being 'greener' than synthetic polymers even although the latter may also be biodegradable. The argument for using renewable resources is that the carbon dioxide burden in the environment is neutral for biologically-based polymers but is positive for polymers based on mineral oil. However, this ignores the oil-based energy that goes into the growing, transport and processing of biological materials to produce polymers. This reasoning is only valid then if the life-cycle utilisation of oil is less for biomaterials than for synthetic polymers. Life-cycle assessment (LCA) [1] of materials provides a useful comparison of the the ecological impact of comparable products. Four major parameters are quantified. The first is *energy consumption*, which includes electrical, thermal and traction power used in extraction, transformation and transportation of raw materials and in the treatment of waste to make it safe in the environment. The second parameter is *air pollution*, and may be estimated as the volume of air that must be added to gas emissions to conform to existing regulations. This includes all gas emissions from raw materials, extraction, production of electrical and thermal energy and in transportation at all stages in the history of the product. Similarly, *water pollution* is the volume of water that should be used to dilute liquid emissions produced over the whole life-cycle of the product. Finally, *waste production*, is the total volume of wastes produced in each stage in the manufacture, use and disposal of the material.

LCA can be used to compare the ecological acceptability of different raw materials, processes and end products. In general there is a correlation between ecological acceptability and cost which is of primary concern to the manufacturer of polymer products. According to the 'polluter pays' principle it must also include environmentally acceptable disposal of by-products as well as the ultimate disposal of the post-user waste. An environmental assay of paper compared with plastics used in packaging shows that twice the amount of fossil fuel is used in the manufacture of paper compared with plastics [1] and the processing of cellulose produces almost twice as much SO_2 and 1.5 times as much NO_x than polyethylene [1,27,28]. Furthermore, when incinerated, paper generates less energy than polyethylene [141 and the latter has a similar calorific value to fuel oil (Table 2) [1]. A full environmental audit should also include the effect on the world's ecology of alternative raw materials. Guillet has calculated [28] that to produce the necessary amount of kraft paper to replace the polyethylene used in carrier bags would require an *additional* 162 million acres of forest land (equivalent to six US states the size of Tenessee). By contrast, land utilisation by all the world's polyethylene plants is negligible. Similar arguments apply to the more recently developed hydro-biodegradable polymers, for example the poly(hydroxyalkanoates) (PHA). These can be made by the fermentation of sugar, but this process is inefficient and hence expensive. Work is currently in progress to genetically modify oilseed rape (*Brassica napus*) to produce seeds containing PHAs. Typically the yield of rape-seed oil ranges from 10–50% and the cost of oils from £0.35–0.83/kg and if 50% yields of PHAs could be obtained prices would be competitive with synthetic plastics. However, it has been estimated that using a more realistic assumption of 30%, yields of PHA, IMha (10^{10} m^3) or 10% of the total area worldwide used to grow oilseed rape would be required to produce enough plastic to satisfy only 7% of the US packaging market [1].

Another hydro-biodegradable polymer, PLA, can also be produced from sugar or corn-starch but even in the case of these plentiful commodities, it is doubtful whether their availability could satisfy the world packaging requirements without the raw material coming into competition with food production. Biological wastes would also cause major problems. It seems inevitable that, even if acceptable yields of polyesters could be obtained from food crops, plastics production would be in competition with food production. In the

long-term, a more acceptable ecological strategy would be to utilise the biological wastes themselves (e.g. molasses or cellulose) to produce biopolymers but this possibility would also require eco-assessment and at present it lies well in the future.

LCA does not consider the suitability of a product for the intended purpose. However, this is a major factor affecting the viability of new biodegradable polymers. Biodegradability is only one of the parameters that affect the acceptability of biologically derived polymers. Biopolymers evolved with inherent environmental biodegradability but by their very nature, they are not custom designed for modern technological use. In fact the more biocompatible a polymer is, the less useful it is as a packaging material. This is why paper has been largely replaced by polyolefins in packaging. The corollary to this is that the greater the chemical modification (esterification) of cellulose to give acceptable technological performance, the less biodegradable it becomes, so that cellophane (40% acetylated cellulose) biodegrades relatively slowly [1]. Similarly, starch is highly biodegradable but it has to be combined with other polymers (e.g. ethylene–acrylic acid or ethylene–vinyl alcohol copolymers) to make it suitable for use in packaging [1,29] and this again reduces its biodegradability. Ultimately, then the usefulness of modified bio-based polymers must depend on balancing adequate technological performance (including in-service durability) and biodegradability.

7. 'Green' polymers in the twenty-first century

The above discussion illustrates conceptually different approaches to 'green' polymer development. Bio-based polymers are based on natural products which are bioassimilated by hydro-biodegradation. However, they have to be made technologically acceptable by chemical modification. The commodity plastics already have satisfactory technological properties but must be modified to become oxo-biodegradable. During manufacture and post-consumer disposal, polyolefins appear to be 'geener' materials than biologically-based polymers. They can be incinerated with heat recovery or mechanically recycled to utilise the 'energy content' of the plastics, provided this is greater than the energy used in the recovery and recycling operations.

Polyolefins with enhanced biodegradability have been available commercially for 25 years and have been used in agricultural products for most of this time. They are bioassimilated by combined peroxidation and biodegradation. Most contain transition metal prooxidants and it has been shown that the peroxidation products are biodegradable [1,16]. Some of these have technological behaviours (processing performance, mechanical properties, etc.) entirely similar to conventional polyolefins and are capable of producing very thin thin films and fibres. The products have wide application in agricultural mulching films, hay binder twines, compostable waste bags and controlled release fertilisers. Future applications currently being evaluated are in agricultural packaging including stretchwrap films for hay and silage, in bird netting and animal feed bags. An essential user requirement in all these applications is a variable but controllable induction time to the beginning of peroxidation which, as in the biodegradation of natural rubber, is the rate controlling step in the overall biodegradation process. In the case of the polyolefins it is very easy to control the rate of peroxidation by the use of environmentally sensitive antioxidants and light stabilisers. This has been discussed in detail elsewhere [15,17–22,25,26].

It is much more difficult at present to control the rate of biodegradation of hydro-biodegradable polymers due to the random nature of microbiological attack in biotic environments. Consequently, these materials are used mainly in the body or in sewage where very rapid biodegradation and mineralisation are required (see Fig. 1). There is some evidence that the degree of crystallinity might be used to control the rate of the biodegradation process [30] but ideally an environment-activated 'trigger' may also be required if these materials are to be used in agriculture or in packaging [1].

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Biomacromolecules

Fall 2001 Published by the American Chemical Society Volume 2, Number 3

Reviews

Programmed-Life Plastics from Polyolefins: A New Look at Sustainability†

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Received June 14, 2001

The term "sustainable" is often assumed to be synonymous with "renewable". However, polymers made from renewable natural resources are not necessarily eco-efficient. Cellulose-based polymers utilize more nonrenewable fossil fuels and are more polluting during manufacture than petro-based polymers. Sustainable polymers also have to be industrially acceptable, and although ultimate biodegradability in the natural environment is important, polymer-based products are required to biodegrade in a controlled way. Service life may be a year or more before the commencement of environmental degradation occurs. Many natural polymers such as rubber, lignin, and humus, like the synthetic polyolefins, biodegrade by an oxidative mechanism (oxo-biodegradation), and consequently much of nature's biological waste cannot satisfy the rapid mineralization criteria currently advocated by standards committees for synthetic polymers. Although biometric tests are more convenient to use than full composting tests, they are meaningless when applied to hydrocarbon polymers, whether natural or synthetic, since oxo-biodegradation is a slower process than hydro-biodegradation at ambient temperatures. Biodegradation standards currently proposed are unrealistic and will need to be modified on the basis of recent scientific evidence.

Technological Advantages of the Polyolefins

Degradable polyolefins have a long history. During the 1970s, a number of products based on polyethylene were commercialized (Table 1). It was recognized at that time that polyolefins as produced were oxidatively unstable in the environment, and early investigations showed that the reason for their instability was the presence of sensitizing impurities in the polymer.[1−4] The most important of these were carbonyl (>C═O)[1,3,4] and hydroperoxide groups (−OOH)[1,5−8] formed during manufacture of plastics products. This led to extensive studies in the polymer industries and later in universities directed toward extending the lifetime of polymers by using heat and light stabilizers.[5−12] The consequent understanding of how the effects of sensitizers resulting from peroxidation could be controlled in polymers was subsequently applied to the opposite problem of accelerating the bioassimilation of polymers in a controlled way after they had served their useful purpose. The development of the degradable polymers listed in Table 1 resulted from these studies.[13−27]

Table 1. Commercial Degradable Polyolefins

photolytic polymers
ethylene−carbon monoxide copolymers: E-CO
ethylene−vinyl ketone copolymers; Ecolyte (J. E. Guillet)
oxo-biodegradable polymers
antioxidant-controlled, transition-metal-catalyzed photo- and thermooxidizable polymers; Plastor (G. Scott−D. Gilead), TDPA (EPI)
PE−starch blends
PE blended with starch (and subsequently with prooxidants)
Coloroll, St. Lawrence Starch (G. J. L. Griffin)

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† Based on a lecture to the 6th International Workshop on Biodegradable Plastics and Polymers, Honolulu, HI, December 12−16, 2000.

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10.1021/bm010099h CCC: $20.00
Published on Web 08/03/2001

Table 2. Energy Used and Pollution Generated during the Manufacture of 50 000 Carrier Bags[a]

environmental burden	polyethylene	paper
energy (GJ) during manufacture	29	67
air pollution (kg)		
SO_2	9.9	28.1
NO_x	6.8	10.8
CH_x	3.8	1.5
CO	1.0	6.4
dust	0.5	3.8
water burden (kg)		
chemical oxygen demand	0.5	107.8
biological oxygen demand	0.02	43.1

[a] Reference 31.

It is relevant to ask why the polyolefins were selected as a basis for biodegradable polymers rather than natural products such as cellulose, already used as cellulose acetate in packaging. Cellulose acetate was known to be slowly biodegradable but suffered from a number of technical deficiencies of which the most important was that the extraction of cellulose from natural products was both energy intensive and polluting. Furthermore, the modification of cellulose by acetylation to give technologically acceptable products sharply reduced the environmental biodegradability of the polymer so that the correct balance between technological acceptability and ultimate biodegradability was difficult to achieve.

By contrast, the polyolefins had already achieved a central position in the distribution of consumer goods because of their combination of flexibility, toughness, and excellent barrier properties, which has made them the materials of choice for packaging applications. They were particularly important in blown film technology and injection moulding because of their ease of conversion and low cost. The present-day efficient distribution of perishable foodstuffs is a direct consequence of the resistance of the polyolefins and other carbon-chain polymers to water and water-borne microorganisms,[25] and in agriculture, the new technology of plasticulture based on polyethylene was already making an impact on the growing of soft fruits and vegetables.[16,20,28,29]

Eco-Efficiency of Petro-Based and Bio-Based Polymers

Three main factors have to be considered when evaluating the life-cycle eco-efficiency of polymers (Figure 1).[30] The first is energy input during manufacture and disposal that is in turn reflected in the life-cycle cost of products. Low energy utilization during manufacture is of course an ecologically desirable objective since it also minimizes carbon dioxide generation. The polyolefins are based on low value oil fractions, and the energy utilized in the production of the same volume container is much lower than for paper (Table 2). The polyolefins can also be recycled for second-life use in a number of ways.[30] If the waste is clean, it can be mechanically recycled, and if incinerated with energy recovery, waste polyolefins have a calorific value almost identical to the oil from which they are manufactured. In this respect, they are less polluting than fossil fuels. As will be discussed below, hydrocarbon polymers also make a positive contribution to compost by biological recycling.

Bio-based polymers such as cellulose and starch are not so conducive to mechanical recycling, and they also have a lower calorific value on incineration. Nevertheless, biomass from energy crops grown on marginal land is an increasingly important source of fuel, and it seems that it may be possible some time in the future to close the energy loop for the manufacture of biopolymers from renewable resources by using fast-growing grasses and soft wood crops as a source of fuel during manufacture thus conserving fossil resources for polymer manufacture (Figure 1).

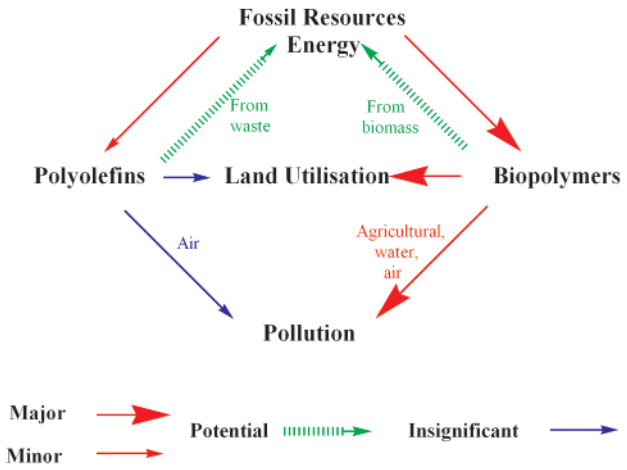


Figure 1. Eco-efficiency of polymers during manufacture and disposal.

The second criterion of eco-efficiency is the minimization of unwanted byproducts and associated pollution (Table 2). This is generally less during the manufacture of polyolefins than during the production of paper.[31] Solid waste and water-borne pollution is particularly severe in the case of agricultural-based polymers. Since the disposal of wastes and the purification of water are themselves energy-absorbing processes, they also contribute to the wastage of fossil resources.[30]

The third factor is land utilization. Although little information has so far been published on the areas and qualities of land that would be utilized if and when bio-based polymers were ever to approach the scale of production of the polyolefins, some reasonable estimates can be made from data already available: If the total U.S. plastics production were to be based on cellulose, a land area equivalent to seven states the size of Michigan, Louisiana, and Virginia would be required.[31] At 30% yield of PHA from an oilseed crop, 7% of the total worldwide land area at present used for the production of oilseed food crops would be required to produce only 7% of the U.S. requirements for packaging plastics.[32]

This suggests that crops for the manufacture of chemicals and polymers would very quickly come into competition with food crops. The argument that plastics could be made from surplus crops is of course parochial, applying primarily to some developed and relatively affluent countries. It is not a basis for the sustainable development of polymers worldwide. By contrast, the land utilization of the petrochemical and polymer industries is negligible in comparison and it seems probable that biopolymers will be restricted to the manu-

facture of speciality polymers, particularly for biomedical applications for the foreseeable future, and that petrochemicals will remain the basis of commodity plastics provided they are environmentally acceptable after discard.

It is clear then that the long-term eco-sustainability of plastics based on renewable resources has not yet been established. It is equally clear that the socioeconomic benefits of the synthetic hydrocarbon polymers also have to be taken into account in comparing synthetic polymers with natural polymers (see below). However, it is instructive to see how the present attitude to synthetic plastics has arisen.

The Popular Image of Plastics

Plastics made from petrochemical feedstocks are portrayed by the "green" lobby as ecologically undesirable because they are made from fossil carbon resources and it is assumed that they are very resistant to biodegradation in the environment. It is ironical that the very physical properties (water and microbe resistance) that have made the polyolefins so commercially successful are a disadvantage when the materials appear in the waste stream.

In the 1960s, a well-known environmentalist, Barry Commoner, suggested that because no biological organisms were known that could attack plastics, the earth would soon be buried in 10 feet of plastics waste! Thirty years later, he expressed the same views in rather a different way when he stated in a report for Greenpeace,[33]

> "Materials made from naturally occurring or biologically produced polymers are the only truly biodegradable 'plastics' available. Since living things construct these materials, living things can metabolise them."

However, many naturally produced materials also persist in the environment for very long periods. For example, certain types of wood such as the sequoia can survive for 500 years in the biotic environment after being felled due to the high concentration of the antioxidant/antibacterial tannin in the bark.[32] Natural rubber (*cis*-polyisoprene) is a hydrocarbon polymer, which oxo-biodegrades naturally in the form of latex as it comes from the rubber tree. However, it can also be synthesized in a chemical plant, and synthetic *cis*-polyisoprene shows exactly the same behavior in a bioactive environment. The same is true of other hydrocarbon rubbers (e.g., polybutadiene) not found in nature. Strikingly, however, both natural and synthetic rubbers after formulation with antioxidants in automotive tires, like sequoia wood, do not detectably biodegrade for many decades in the outdoor environment. This is because the antioxidants added during manufacture inhibit the formation of low molar mass oxidation products that are absorbed and utilized as a source of energy by bacteria and fungi. The nonbiodegradability of commercial rubber products is then not a consequence of the nonbiodegradability of the rubber molecule whether natural or synthetic but of the inhibition of its oxidation by antioxidants.[32]

Polyolefins are hydrophobic hydrocarbon polymers similar to the rubbers, and like the rubbers, they are very resistant to peroxidation and biodegradation as commercial products due to the presence of antioxidants and stabilizers.[34−36] They are also highly resistant to hydrolysis, and for this reason they cannot hydro-biodegrade. However, it has been shown that they can be made oxo-biodegradable by the use of prooxidant additives[11−17,19−27,32] leading to hydrophilic surface modification friendly to microorganisms that are thus able to bioassimilate the low molar mass oxidation products (see below).

Balancing Environmental Acceptability against Technological Utility

The polyolefins and the polysaccharides stand at the opposite ends of a spectrum of polymer properties (Figure 2).

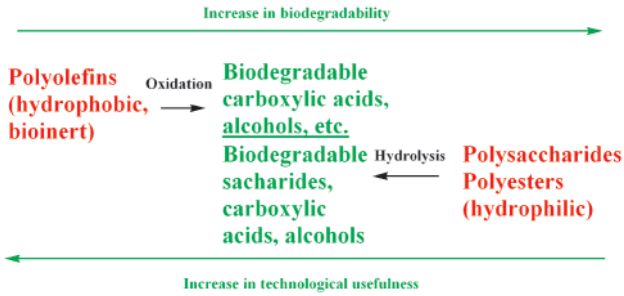


Figure 2. Technologically and environmentally acceptable polymers from polyolefins and natural products.

The naturally occurring hydro-biodegradable polymers such as cellulose, starch, and so forth are water wettable or water swellable. Consequently, to be technologically useful, they have to be made less hydrophilic with sacrifice of biodegradation rate. The properties of synthetic hydrocarbon polymers are a mirror image of this.[25] They are resistant to water, which is their main attribute in packaging, but in their conventional commercial versions, they do not biodegrade at a practically acceptable rate in the natural environment and they in turn have to be made more oxo-biodegradable by prior thermo- or photooxidation. Between these two extremes are the hydro-biodegradable aliphatic polyesters such as polylactic acid (PLA) and the poly(hydroxyalkanoates) (PHA). These, like the hydro-biodegradable polysaccharides are on a "knife-edge" balance between the achievement of useful technological performance and end-of-life biodegradability. The polyolefins, by contrast, can be given a programmed lifetime by the use of antioxidants. Sustainability must in practice be a compromise between commercial viability (i.e., cost-performance) and environmental acceptability. This must ultimately mean adaptability, namely, the potential for adapting polymers (both bio-based and petro-based) to the needs of the environment and to the needs of society. Bio-based polymers have already found important niche applications (for example in medicine) where cost is much less important than function. However, cost with environmental acceptability will continue to dominate the consumer market, and it seems very unlikely that biodegradable petro-based polymers will be displaced from their current role in packaging and agriculture.

Programmed-Life Polyolefins

It is implicit in the above discussion that bioassimilation of plastics residues in the environment is an essential but not the only requirement of technologically useful packaging plastic. In most cases, plastics require a controlled lifetime before physical degradation commences. Figure 3 shows the behavior of an ideal degradable plastic.

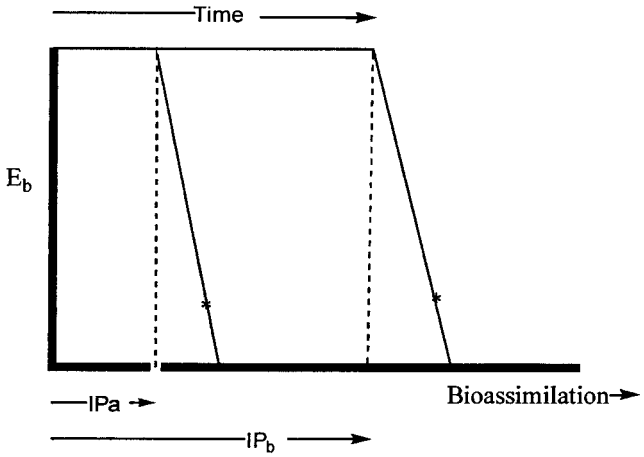


Figure 3. The ideal behavior of a degradable plastic in the environment (ref 32). E_b = elongation at break; IP_a and IP_b are induction periods during which no change in chemical, physical, or mechanical properties should occur; * is the point at which the sample disintegrates (generally ~85−90% loss of E_b).

There should be no change in the physical and mechanical characteristics of the polymer during the induction period (IP). Moreover, the IP must be variable (IP_a, IP_b) and controllable in the end environment if the full potential of the plastics is to be realized.[23] Photolysis and thermolysis of peroxidation products (notably, >C=O and POOH) is the primary cause of the loss of mechanical properties of hydrocarbon polymers in the environment.[1,10,14,21,23,24] In many applications and particularly in plasticulture, mulching films and tunnels used to control the microenvironment of the plant[20,28,29,32,34−36] must be timed to disintegrate (E_b < 10%) under slight pressure at the end of their useful life. If the films break too early, there will be a significant loss in crop yield, and if they break down too late the partially degraded plastic will clog the automatic harvester.

The photographs in Figure 4 illustrates two different grades of polyethylene mulching film that differ only in the induction period before physical disintegration commences. In this case, the IP of #131 is 5 times that of #221 which enables a second crop to be grown over the same film the following season. The subsequent physical fragmentation and ultimate bioassimilation occurs at a similar rate.

Many auxiliary plastics products used in agriculture and horticulture also require an extended lifetime before losing mechanical strength. Important examples are polypropylene baler twines, polyethylene stretch-wrap silage films, bird protective netting, and agricultural packaging.[32] It is crucially important then to understand how the hydrocarbon polymers degrade in the environment by a combination of peroxidation and bioassimilation and how the free radical chain mechanism can be controlled by antioxidants.

Figure 4. Programmed-life mulching films in Taiwan. Printed with the kind permission of Dr. S-R. Yang at the Tainan District Agricultural Station.

Products Formed by Peroxidation of Polyolefins

The mechanism of abiotic peroxidation of hydrocarbons has been extensively studied over the past 50 years.[1,2,5,8−12,33−35,48] The primary products of the peroxidation chain reaction in (1) and (2) are hydroperoxides which either thermolyze (Δ) or photolyze ($h\nu$), particularly in the presence

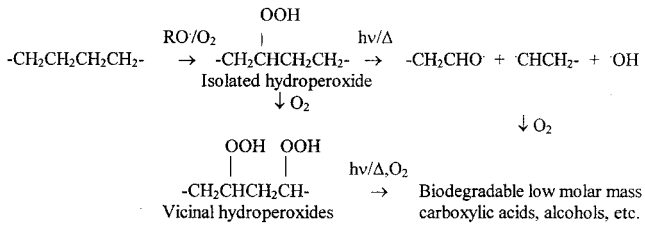
$$P^{\cdot} + O_2 \rightarrow POO^{\cdot} \quad (1)$$

$$POO^{\cdot} + PH \rightarrow POOH + P^{\cdot} \quad (2)$$

of transition metal ions (see below) with chain scission and the production of biodegradable low molar mass oxidation products such as carboxylic acids, alcohols, aldehydes, and ketones (Scheme 1). Many of these oxidation products are lost by volatilization during thermal oxidation in an open atmosphere, and carbon dioxide has been recognized to be a significant product under these conditions.[38−44] Albertsson, Karlsson, and co-workers have recently paid particular attention to the low molar mass products, and a wide range of carboxylic acids, alcohols, hydroxy alcohols and esters, and low molar mass hydrocarbon waxes have been identified in the thermal and photooxidation of commercial degradable polyethylenes.[43,44] The process involves the formation of vicinal hydroperoxides by the well-established "back-biting" mechanism,[45,46] and in the case of polypropylene, 90% of

the hydroperoxides are present as hydrogen-bonded vicinal hydroperoxides.[45] However, both isolated (non-hydrogen-bonded) and vicinal (hydrogen-bonded) hydroperoxides are present in polyethylene, and Albertsson et al. have concluded that the same mechanism is responsible for the low molar mass biodegradable products they have identified during peroxidation of PE.

Scheme 1. Formation of Biodegradable Carboxylic Acids by Peroxidation of Polyethylene



An interesting consequence of the above mechanism is that in the presence of microorganisms the concentration of carbonyl compounds is very much reduced,[43] indicating that they are assimilated by the microbial cells as they are formed. This is consistent with the findings of Lemaire, Scott, et al.[47] that microorganisms can utilize oxidized polyethylene as the sole source of carbon, leading to bioerosion of the polymer surface while leaving M_w of the bulk plastic essentially unchanged.

As mentioned earlier, antioxidants inhibit the chain reaction that leads to hydroperoxide formation and the subsequent biodegradation of hydrocarbon polymers.[32,34,35] Thus, chain-breaking (hindered phenol) antioxidants inhibit the oxo-biodegradation of the polyolefins under thermooxidative conditions during service. However, to simply omit antioxidants and stabilizers during conversion to commercial products is not a viable technological solution to the environmental persistence of hydrocarbon polymers since they are added to protect the polymer against mechanooxidation during the processing operation and to provide the required shelf life.[48] Furthermore, commercial processing stabilizers such as the hindered phenols or phosphite esters considerably extend the life of the polyolefins in the outdoor environment[49] even though they are not normally considered to be light stabilizers.

It has been known since natural rubber became a technological product that many transition metal ions are effective accelerators for peroxidation and hence for the biodegradation of the hydrocarbon polymers (Scheme 2) and that this can be retarded by certain types of antioxidant.[5,37,50,51] Hindered phenols control the metal-catalyzed melt degradation of polyolefins during processing but are relatively ineffective in controlling photodegradation.[51] Photodegradable polyolefins based on transition metal compounds and processing stabilizers are thus very effective in short-term applications such as garden waste bags that are intended to biodegrade in aerobic compost but not in programmed-life products such as mulching films, silage film, or baler twines where an outdoor service life of up to 12 months may be required. Some of the naturally occurring oxygenases (e.g., Cytochrome P450) act in a similar way to initiate an abiotic peroxidation process, and this has been shown to occur when polyethylene contains no protective antioxidant.[22] The evidence suggests that the combination of abiotic and biotic initiation of peroxidation causes a cooperative bioassimilation of the polymer.

Scheme 2. Iron Catalyzed Peroxidation of Hydrocarbon Polymers[a]

$$Fe^{2+} + POOH \rightarrow Fe^{3+} + PO\cdot + OH^- \quad (3)$$

$$Fe^{3+} + POOH \rightarrow Fe^{2+} + POO\cdot + H^+ \quad (4)$$

$$POO\cdot + PH \rightarrow POOH + P\cdot \xrightarrow{O_2/PH} POOH \quad (5)$$

$$PO\cdot + PH \rightarrow POH + P\cdot \xrightarrow{O_2/PH} POOH \quad (6)$$

[a] PH = hydrocarbon polymer, POOH = macromolecular hydroperoxide.

Since the sequence of reactions shown in Scheme 2 leads to the rapid buildup of hydroperoxides in the polymer, peroxidation cannot be controlled by chain-breaking antioxidants such as the hindered phenols since the latter are rapidly destroyed by hydroxyl and peroxyl radicals. By contrast, some peroxidolytic antioxidants such as the metal dithiocarbamates, $(R_2NCSS)_2M$, are able to catalytically destroy hydroperoxides as they are formed in the polymer in a process not involving the formation of radicals.[9−12,16,22] Consequently, peroxydolytic antioxidants based on transition metal ions inhibit peroxidation until the antioxidant has been depleted by the action of light or heat, liberating the prooxidant metal ion in a controlled manner. This process has been discussed in a number of reviews of antioxidant-controlled biodegradation of carbon-chain polymers[15−17,23,32,34−36] and will not be discussed further here.

The Effect of the Biodegradation Environment

The two alternate mechanisms of polymer biodegradation, summarized in Figure 5, cut across the biopolymer−petropolymer divide. Hydro-biodegradation is the well-known process that gives bioassimilable products from cellulose, starch, polyesters, etc. Oxo-biodegradation also leads to the generation of biodegradable carboxylic acids, alcohols, ketones, etc. by peroxidation, initiated by heat or light. It should be noted that although photolysis of C═O modified polymers is a precursor to peroxidation in the case

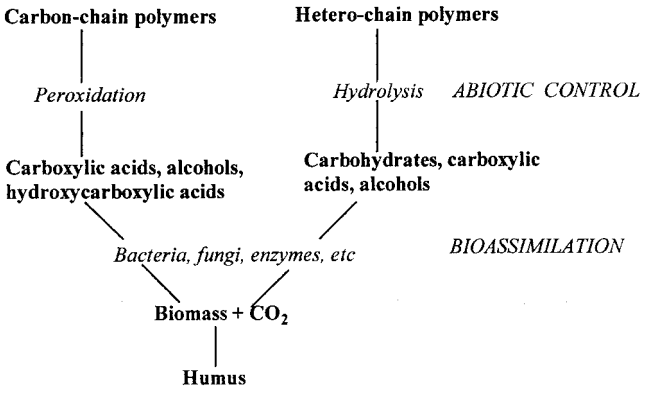


Figure 5. Alternate mechanisms for the biodegradation of the synthetic polymers (ref 32).

of the Ecolyte polymers,[31] E-CO plastics do not appear to biodegrade rapidly after photolysis.[47]

Like the hydrolysis products from hydro-biodegradable polymers, the low molar mass oxidation products formed by peroxidation of the polyolefins can also be utilized by microorganisms as nutrients to produce cell biomass.[43,44,47,52] Rubbers, if they do not contain antioxidants, oxo-biodegrade much more rapidly than the polyolefins. Aliphatic polyesters are more oxidatively stable, but they are hydrophilic and are hydrolyzed and bioassimilated rapidly in an aqueous biotic environment in much the same way as starch and cellulose.

The development of standard tests to measure the rate of biodegradation of polymers is necessary in order to ensure that residues from plastics packaging do not create a long-term pollution problem in the environment. Unfortunately, carbon-chain polymers, including many natural products, do not pass the tests laid down by the American Society for Testing Materials (ASTM) in the U.S. and Comité Européen de Normalisation (CEN) in Europe. Quite unscientific explanations are put forward to explain why synthetic polymers, but not natural polymers, must be shown to be mineralized within a very short time, for example, in compost. It is argued that there is no need to demonstrate that natural materials such as leaves and twigs (which contain the relatively slowly oxo-biodegrading lignin) do not need to mineralize during composting but that synthetic hydrocarbon polymers are "different".[54] The following rationale is given by CEN to explain why this distinction can be made.

> "Natural products (leaves, wood, small stones are...generally known to be non-toxic. They are universally recognised as biodegradable. On the other hand, residues of synthetic polymers would be perceived by the general public as being contamination of the compost"

The basis for this statement is that

> "The accumulation of lignin in the environment is a natural event which is beneficial for the fertility of the soil. On the other hand, the accumulation of other foreign materials cannot be encouraged because, while it is well known that lignin is ultimately degradable and helps environment and soil structure, this cannot be claimed for synthetic products whose behaviour in the environment is not known"

From this, it is reasoned that

> "the CEN scheme considers lignin and the natural non-chemically modified materials as biodegradable *by definition*"

This extension of the popular views of Greenpeace discussed above is not a good basis for the development of science-based standards. In particular, it ignores the extensive studies on the oxo-biodegradation of polyolefins. Nor does it recognize that lignin, a major constituent of natural products, is also an oxo-biodegradable polymer similar in structure to the synthetic phenol-formaldehyde resins and like the latter, it is very stable due to the presence of the polyphenolic antioxidant functions in the polymer chain. Thus, polyethylene, PF resins, lignin, humic acid, and tannic acid oxo-biodegrade relatively slowly but all are ultimately converted to carbon dioxide and water. Humus is a complex mixture of polyphenolic and quinonoid compounds, and the slower mineralization occurs, the more beneficial is this organic matter to the fertility of the soil.

The Time Scale for Bioassimilation into the Environment

Biodegradable plastics may end up in sewage systems, in compost, or on the soil as litter (Figure 6). The CEN standard for synthetic polymers in compost, EN 13432, stipulates that they must be substantially (i.e., >90%) converted to carbon dioxide and biomass in an aqueous biotic environment within 6 months.[55] This is to simulate the behavior of pure cellulose which is rarely found as such in nature. The presence of lignin in natural products such as leaves and twigs slows down this process in an ambient biotic environment for the reasons already discussed.

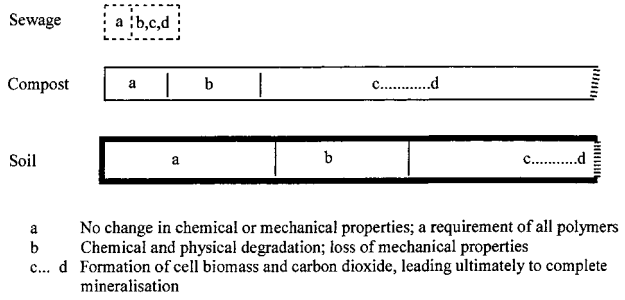


Figure 6. Biodegradation time scale for polymers in different environments (ref 32).

A good deal of packaging based on cellulose in combination with lignin and/or other bonding agents does not satisfy this requirement, raising serious doubts about the ecological validity of this test.

In reality, rapid mineralization brings no benefit to compost or to the soil since it increases the CO_2 "greenhouse" effect. Rapidly mineralizing polymers are not therefore "recoverable" in the sense required by the European Directive since carbon dioxide is not a useful product. Rapid mineralization is thus a waste of resources, and to make it a requirement that synthetic polymers entering the compost or soil environment must be rapidly mineralized is ecologically counterproductive.

The proposed standards are causing a great deal of concern to manufacturers of degradable polyolefins because of their arbitrary nature. No oxo-biodegradable polymers including those found in nature can possibly pass the mineralization test demanded by EN 13432. The effect of this standard will be to discriminate in the future against the manufacturers of degradable hydrocarbon polymers throughout the countries of the enlarged European Union. At the same time, it will favor less ecologically efficient bio-based polymers with consequent detrimental effects on the environment.

A number of specialists in polymer degradation have pointed out that EN 13432 does not take into account research carried out during the past 10 years on the biodegradation of the polyolefins. Laboratory biometric tests are based on CO_2 evolution or oxygen absorption at ambient

temperatures in an aqueous environment. These tests (e.g., the Sturm test) were originally developed to evaluate the biodegradability of aqueous detergents, and while they are entirely satisfactory for characterizing polymers that have to biodegrade rapidly in sewage systems (Figure 6) they are not effective in characterizing the behavior of polymers in compost at elevated temperatures. The compost environment accelerates the peroxidation of the oxo-biodegradable polyolefins and also permits the assessment of ecotoxicity on the final product in the field under real conditions. Equally important tests are laboratory measurement of abiotic peroxidation and the rate of subsequent bioassimilation of low molar mass oxidation products. These provide complementary information that can be used to assess the time scale for ultimate absorption of the polyolefins into the environment. The following is an excerpt representing the views of scientists active in the field of polymer degradation.[56]

> "Biodegradability tests that have been developed largely reflect the behaviour of hydro-biodegradable polymers (e.g. aliphatic polyesters, modified starch). These materials are ideal for rapid biodegradation in sewage sludge where a maximum rate and extent of mineralisation is required. The fundamental characteristic and most positive value of compost or mulches is the presence of biomass. Without biomass, there simply would be no product.
>
> "Rapid mineralisation is not ideal for polymers in compost where the carbon in the original plastic should be converted over a longer period of time to biomass and only slowly to carbon dioxide. The oxo-biodegradable polymers (e.g. the polyolefins) are ideal for this purpose since controlled peroxidation is the *rate-determining* step in the overall process. Furthermore they cannot give toxic or otherwise objectionable by-products during bioassimilation"

Similar concerns have been expressed by the European Commission Directorate for Industry and the Environment.[57]

> "ISO 14851 (0xygen consumption) and ISO 148 (Sturm test) do not simulate composting conditions
>
> "What is really needed is to know what is the fate of materials under composting conditions and what happens once it is released to the soil
>
> "If the packaging material does not completely biodegrade during the composting process, it should be demonstrated that it eventually degrades in the soil"

This demands an early revision of EN 13432 to take into account scientific studies on the biodegradation of polyolefins carried out during the past eight years. This should be based upon the hierarchy of tests shown in Table 3 and the scientific basis for them.

A number of basic scientific studies have already been published which are relevant to the oxo-biodegradation of polyethylene in the environment. For example, it has been shown that soil bacteria and fungi can utilize peroxidized polyethylene in the absence of any other source of carbon leading to bioerosion of the polymer surface.[47] Biometric tests (oxygen absorption) have confirmed that the thermal peroxidation products formed on the surface of the polymer are rapidly mineralized.[52] There is also growing evidence that polyethylene can biodegrade in the body.[58,59] Studies are currently in progress to correlate the extent of peroxidation of polyolefins with polymer weight loss both during abiotic and biotic assimilation processes.

Table 3. Hierarchy of Tests

full scale composting trials
particle size reduction
visual impact
ecotoxicity measurements
plant germination and growth rate
accumulation of transition metals in stems, leaves and fruit
effect on macroorganisms (worms, daphnia, etc.)
background scientific studies
rate of abiotic peroxidation at composting temperatures
rate of biomass formation and polymer weight loss
biometric measurements on peroxidized polymer
correlation of bioerosion with extent of peroxidation

Conclusions

Nature uses a combination of abiotic and biotic processes to return its own waste to the natural carbon cycle. Abiotic peroxidation and hydrolysis of man-made polymers normally precede the bioassimilation of low molar mass products in the environment. Consequently, International Standards must reflect this fact and incorporate the relevant abiotic processes into test methods and protocols.

The polyolefins have been shown to satisfy the same oxo-biodegradability criteria that characterize biopolymers such as natural rubber and lignin, and as they are more eco-efficient during manufacture and effective during use than bio-based polymers, it seems certain that they will remain the materials of choice for packaging and agricultural applications.

Acknowledgment. We are grateful to Dr. S-R. Yang for permission to reproduce the photograph in Figure 4 and to Professors L. Costa and R. Wasserbauer for helpful discussions about the biodegradation of polyethylene in vivo.

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BM010099H

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Polymer Degradation and Stability 91 (2006) 1581–1592
Polymer Degradation and Stability
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Polyolefins with controlled environmental degradability

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Received 31 July 2005; accepted 13 September 2005
Available online 28 November 2005

Abstract

Antioxidants and stabilisers, developed to increase the durability of polyolefins, in combination with prooxidant transition metal complexes provide industrial products with widely variable but controlled lifetimes. The low molar mass oxidation products formed during photo-oxidation and thermal oxidation are biodegradable and oxo-biodegradable polyolefins are now widely used in agricultural applications and in degradable packaging as examples. The scientific basis for the performance of oxo-biodegradable materials is explained with reference to naturally occurring macromolecules. Comparison with hydro-biodegradable materials is made and the need is demonstrated for performance standards to be developed that mimic nature's resource recovery mechanism, that of oxo-biodegradation.

Keywords: Oxo-biodegradable polyolefins; Peroxidation; Prodegradants; Antioxidants; Mulching films; Compostable packaging

1. Introduction

It is generally recognized that polyolefins are bioinert, that is, they are highly resistant to assimilation by microorganisms such as fungi, bacteria and the like. This is not surprising since the surfaces of materials and articles made from polyolefins are hydrophobic and thus inhibit the growth of microflora on them. Moreover, there are common mechanisms of biodegradation that involve bioassimilation from the ''ends'' of substrate molecules. Since commercial polyolefins have relatively high molar mass values, there are very few ends of molecules accessible on or near the surfaces of materials made from these resins. It has been observed, however, that the oxidation products of polyolefins are biodegradable [1–7]. Such products have molar mass values that are significantly reduced, and they incorporate polar, oxygen-containing groups such as acid, alcohol and ketone [8]. This is the basis for the term oxo-biodegradable polyolefins. This concept is used to distinguish polymers that biodegrade by a hydrolysis mechanism from those that are inert to hydrolysis but undergo oxidation [9,10]. Oxo-biodegradation then denotes a two-stage process involving, in sequence, oxidative degradation, which is normally abiotic in the first instance, followed by the biodegradation of the oxidation products. It should be noted that, considering for the moment a given piece of polyolefin plastic in a microbially active environment, abiotic and biotic degradation will be occurring simultaneously owing to the normal range of molar mass values in commercial materials. The sequence of oxidative degradation followed by biodegradation applies to individual molecules. In reality, as each molecule undergoes oxidative degradation and is reduced in size, a point is reached when microbial degradation will commence. This situation conforms to the definition [10] that a biodegradable polymer is one ''in which degradation is mediated at least in part by a biological system''.

The rate-determining part of the two-stage process in oxo-biodegradation is the oxidation segment, commonly called peroxidation. It has been demonstrated [1–11] that the biodegradation of polar molecular fragments from polyethylene (PE) occurs relatively rapidly. However, in the conditions in which they are normally employed and disposed of, commercial polyolefin products used for packaging, for example, undergo peroxidation quite slowly. This is because of the presence of antioxidants and other stabilisers, and the

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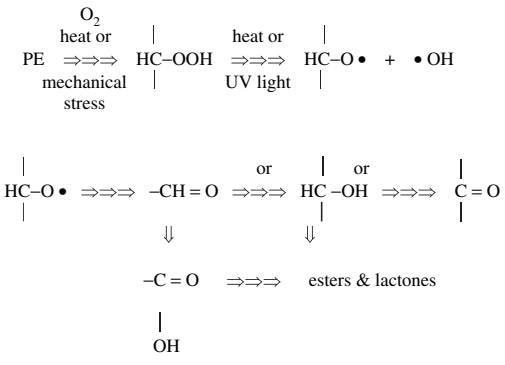
0141-3910/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2005.09.010

relatively benign conditions in landfills into which many used plastics are dumped. Moreover, conventional plastics are a real problem in commercial composting operations because they do not undergo abiotic oxidation very rapidly even at the elevated temperatures encountered, and they cannot biodegrade as a result. The persistence of normal industrial plastics causes a visual problem in the compost product and reduces its applicability and hence its commercial value. In addition, although the use of PE as agricultural mulch film is common, the requirement for mechanical property retention by the films until at or near harvesting time, followed by rapid embrittlement [11] cannot be met by simply omitting or even just adjusting the content of the stabiliser(s) added to the resin prior to fabrication. What is needed is a way of controlling the time during which the polyolefin retains its normal, useful properties as well as a way of having it undergo subsequent oxo-biodegradation at a much higher than normal rate that is commensurate with the application and with the disposal environment. The key to this control requirement is a sound understanding of the peroxidation mechanisms and kinetics.

2. Abiotic oxidation of polyolefins

Research stretching back several decades [12–14, and references therein] has established the sequence of reactions that are regarded as the essence of polyolefin peroxidation. Although the products of the oxidation initiated by heat are similar to those resulting from photo-oxidation, it was investigations of the latter which confirmed that it was the presence of sensitising impurities, generated during the fabrication of polyolefin products, that caused the instability of these plastics in the environment [15]. The most significant of these impurities are carbonyl groups [12,15–17] and hydroperoxide groups [12,15,18–20] with the latter of particular importance as a consequence of thermo-oxidation during processing. Scheme 1 illustrates one way of describing the formation of some of the products generated as a result of the peroxidation of PE. The starting point is shown here as a hydroperoxide, the formation of which resulted from shear stresses during extrusion, for example, that caused homolytic bond cleavage. The resultant carbon-centred radical reacted with the oxygen that is never removed completely from the system to form a peroxyl radical which, by hydrogen abstraction, is converted to a hydroperoxide group. This group is unstable to both heat and UV light, and its destruction will lead to the formation of several types of oxygen-containing products. One of the few differences between peroxidation initiated by heat and by light is that ketone products are stable to heat but not to UV light. In either case, one is dealing with a branching chain reaction sequence in which the reaction of the hydroperoxide group is the rate-determining step in peroxidation leading to molar mass reduction. Scheme 1 shows only a part of the reactions relevant to the oxidising system. The formation of low molecular weight biodegradable fragments is discussed in Section 5. However, the reader wishing more details on abiotic degradation is encouraged to consult Refs. [12,13,20,21, and references therein].



Scheme 1. A simplified scheme that illustrates the degradation, by peroxidation, of PE.

In order to focus on polyolefin disintegration, it is necessary to identify those parts of the overall peroxidation process that result in the breaking of C–C bonds in the main polymer backbone. Examples are the beta-scission of the alkoxyl radical (Scheme 1) to produce ketones and aldehydes, which are subsequently oxidised to form carboxylic acids.

Since the properties of PE (and other macromolecular materials) derive in large part from the relatively high molar mass values of the original molecules, molar mass reduction will lead to a reduction in elongation at break (EAB) and to a major reduction in tensile breaking strength. A PE film may, as formed, have an EAB value of 500% or more. After molar mass reduction resulting from significant peroxidation, however, the EAB will have fallen drastically. At less than 5% EAB of the original film, it is considered to be brittle and will fragment even with gentle handling.

3. Controlling peroxidation

It will be evident from the above that although biodegradable plastics are required to disintegrate rapidly followed by biodegradation at the end of their use life, it is equally important that their mechanical properties remain essentially unchanged during use. The rate of peroxidation of hydrocarbons, including polyolefins, depends on two primary parameters. The first is the rate of the free radical chain reaction of the polymer with oxygen, which is in turn governed by the rate of reaction of peroxyl radicals with polymers [12].

$$PH + POO\bullet \rightarrow P\bullet + POOH \quad (1)$$

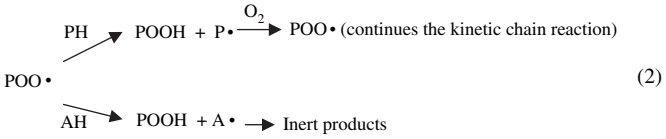
where PH = polymer.

The second is the presence of initiators that lead to the formation of radicals, of which the most important are the hydroperoxides (POOH) that are the products of the chain reaction. From this it follows that antioxidants and stabilisers also fall into two categories; the *chain-breaking antioxidants* that deactivate alkylperoxyl radicals and the *preventive antioxidants* that destroy hydroperoxides or otherwise neutralise their action [22].

3.1. Chain-breaking antioxidants

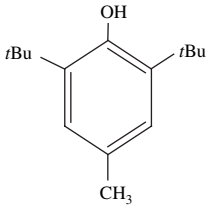
Chain-breaking antioxidants can act by two complementary mechanisms.

(a) The *chain-breaking donor* (CB-D) antioxidants, depicted typically as AH, are generally phenols or arylamines that reduce alkylperoxyl radicals more rapidly than the latter can abstract a hydrogen from the substrate (PH), Reaction (2) [12]. A primary requirement is that the aryloxyl or aminoxyl radical ($A^{\bullet}$) produced should not continue the kinetic chain, Reaction (2). This is normally achieved by delocalisation of the unpaired electron in the aromatic ring and/or by steric hindrance of a group formally containing the unpaired electron.



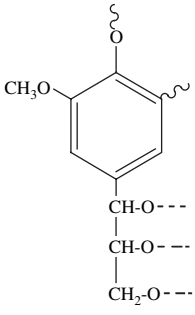
(2)

It is the combination of electronic and steric mechanisms that make the 2,6-di-*tert*-butyl phenols (e.g. BHT) so effective as antioxidants [12,21,22].

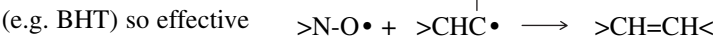
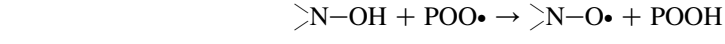


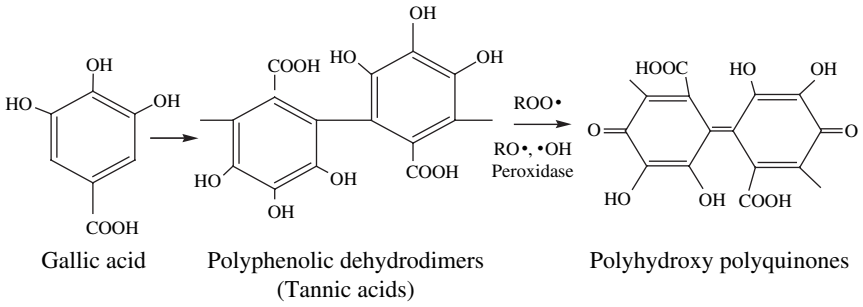
BHT

CB-D antioxidants are widely distributed in biological systems to protect substrates that are susceptible to peroxidation from attack by atmospheric oxygen [23]. The best known of these, because of its therapeutic value, is α-tocopherol, which is not a hindered phenol but does form a highly delocalised aryloxyl radical [23]. Other less well-known biological antioxidants that are present in natural products in very large quantities are the polyphenolic natural products such as lignin, the second most abundant polymer on the planet. Lignin contains a high concentration of aromatic structures linked through −C−O− and −C−C− bonds.



Lignin monomeric unit

~~~ indicates potential sites through which dehydropolymerisation and cross-linking may occur.

----- indicates sites through which attachment to cellulose may occur.

Some of the hydroxyl groups in lignin are phenolic and the lower molar mass lignins are very powerful antioxidants that protect the lignocellulose substrate from destruction by molecular oxygen of the environment [24,25]. The lower molecular weight extracts of lignin have been shown to be effective antioxidants in polypropylene [26].

Another group of naturally occurring antioxidants is the tannic acids (tannin), which are biosynthesised from gallic acid by oxidation, Reaction (3) [27]. They contain up to three phenolic hydroxyl groups in the same aromatic ring and are consequently highly effective stabilisers for lignocellulose with which they are normally associated in nature. The outstanding durability of the ''red-wood'' sequoia trees is primarily due to the presence of high concentrations of tannic acids in the bark [28], the colour of the acid gives them their name (Scheme 2).

(b) The *chain-breaking acceptor* (CB-A) antioxidants are oxidising agents. More specifically they are ''stable'' radicals such as aminoxyls (>N−O•), which remove a hydrogen from the propagating radical to give a stable molecule, Reaction (3). An important commercial example is the cycloaliphatic hindered aminoxyls that are reversibly reduced by carbon-centred radicals and continuously re-oxidised by peroxyl radicals, Reaction (4) [15,22,29,30].



(3)



(4)

This type of chain-breaking antioxidant is particularly effective in the presence of UV light since aliphatic aminoxyls are not destroyed by the short wavelength of the sun's spectrum and the deactivation cycle continues over very many cycles until the redox (catalytic) system is slowly destroyed by side reactions [15,30]. For normal commercial polymers, this is a considerable advantage but it is a disadvantage in light-controlled photodegradable antioxidants where rapid disintegration is required at the end of the service life of the artifact (see Sections 3.2 and 4.2).

3.2. Preventive antioxidants

Peroxidation is normally initiated by the external environment and initiation involves a number of processes giving rise to free radicals. The most important of these are as follows.

(a) Photolysis or thermolysis of unstable compounds, of which hydroperoxides and ketones in the polymer structure (Section 2) are the best known photo-initiators. Consequently, the *peroxide decomposing* (PD) antioxidants are the most important preventive antioxidants [22].
(b) Transition metal ion catalysed hydroperoxide decomposition can be inhibited either by removing the hydroperoxides (see (a)) or by *metal deactivation* (MD), which generally involves metal ion chelation [31].
(c) Photolysis of hydroperoxides can be reduced or eliminated by the PD process or by screening the incident UV light. The latter is normally effected by light-stable *UV absorbers* (UVAs) [15] or by pigments such as carbon black and titanium dioxide, which screen the polymer from UV light.
~~~



Scheme 2. Biosynthesis and antioxidant function of the tannins.

In order to control both the lifetime of a degradable plastic during use as well as the rate of subsequent biodegradation in the environment, the onset of pro-oxidant activity must be controlled by appropriate antioxidants. Since the most successful pro-oxidants currently in use are transition metal ions that catalyse the decomposition of hydroperoxides, this can be achieved by the process (b) above. The successful use of such systems, particularly in plasticulture, has been widely discussed in the technical literature [3,8,9,22,32–37].

Some antioxidants act in cooperation to give the phenomenon of *synergism* [38]. In practice synergism is often achieved by the dual functionality of a single compound. For example some metal complexing agents are both MDs and PDs, resulting in the phenomenon of *autosynergism* [38]. Thus light-stable transition metal dithiocarbamates $[R_2NCSS]_2M$ (e.g. when M = Ni, Co, Cu) are among the most powerful PD/MD antioxidants known [10,15]. With other transition metal ions, notably Fe, the metal complexes are highly effective ''delayed action'' photo-sensitisers [32]. In this case the ''inversion'' process from stabiliser to ''activator'' is facilitated by light and this system has been used for many years in agricultural mulching films [8,9,34,35] and in photo-biodegradable polypropylene twines.

4. Microbiology applied to waste reduction: specific disposal environments

Control of the lifetime of polyolefin plastics comes with control of the onset of peroxidation and the rate at which it occurs subsequently. Antioxidants, UV stabilisers and other protective additives have in the past been developed to improve the long-term durability of polyolefins, particularly in the out-door environment. Today the understanding of the basic science of oxidative degradation permits the use of these same additives in combination with prodegradant metal ions in polyolefins in applications for which a short but controlled lifetime is required. In general it is essential that the polyolefin retain its useful properties through one or more of a variety of fabrication procedures, e.g. blending, pelletising, extrusion, and injection moulding. The final product – film, bag, container, etc. – must have a reasonable storage life. And, of course, the customer expects to have a functional material or article that serves a useful purpose under a variety of circumstances. It is at the end of the service life that the controlled-lifetime polyolefin must degrade in whatever environment it is discarded. As has been noted already, peroxidation of the plastic must begin after a specific use-time and should proceed relatively rapidly. The optimisation of the use-time/time-to-(bio)degrade ratio is best identified in terms of specific applications and these, in turn, involve specific disposal environments.

4.1. Litter

It is an unfortunate fact that packaging plastics (films, bags, bottles, etc.) are discarded carelessly outdoors after use by thoughtless people. Industrial plastic litter arises from the agricultural, shipping and fishing industries. Much of this litter is made of polyolefins, and it persists as an eyesore (or worse) for many months or years [10,39–41]. The high costs of collecting and disposing of discarded plastics preclude such activities in any consistent and widespread way. Careless and avoidable litter, particularly in urban areas should be controlled primarily by legislation and public education and degradable packaging should be employed as a safety net to reduce the accumulation of plastic litter. The use of oxo-biodegradable polyolefins and particularly those which photodegrade in a controlled way followed by rapid bioassimilation can reduce or eliminate many chronic litter problems and is particularly valuable in places of high ecological significance, which are generally remote from centres of population (e.g. on the seashore or in the countryside). Early examples of this concept were copolymers which included a ketone carbonyl group alpha to the main chain [17,39,42], described as the Ecolyte™ process. Vinyl ketones were copolymerised with specific vinyl monomers to produce plastics having much greater sensitivity to terrestrial sunlight than the analogous homopolymer plastics containing no ketone groups. The same principles were applied to make photosensitive condensation polymers. Other examples of commodity plastics with enhanced sensitivity to oxidative degradation initiated by near-UV radiation are the ethylene–carbon monoxide copolymers [43]. These plastics are commonly used for the loop carriers for beverage-can 6-packs. Photosensitive co-polyolefins as described here begin to undergo peroxidation upon exposure to terrestrial sunlight at a rate that is adjustable by controlling the ketone content.

The use of additives, rather than the copolymer approach described above, has been shown to provide the necessary control of the shelf life, use life and degradation time for polyolefin products in a variety of applications. The first of these that really did provide controlled lifetimes was the Scott–Gilead technology [44]. It was demonstrated more than 30 years ago [45,46] that some metal complexes are efficient photo-pro-oxidants for polyethylene which, when photo-oxidised, not only fragment but the oxidation products biodegrade in any biologically active medium.

Another technology that addresses the litter problem is based on the work of EPI, Environmental Plastics Inc. Once again, an additive approach is used. TDPA® formulations added to polyolefins provide for conventional fabrication techniques, controlled storage- and use-lives and relatively rapid oxidative degradation after disposal [47]. All these time periods can be controlled by altering the additive formulation to suit different applications and different disposal conditions in a variety of geographic locations.

There may be readers who regard the use of oxo-biodegradable plastics as potentially encouraging the litterers amongst us, and who prefer the use of ''education'' and fines to address the problem. This concern is unfounded. Guillet has published [39] an analysis of this problem and has shown that ''the most effective way to deal with the litter problem is by reducing the 'lifetime' of the littered object''.

4.2. Agricultural plastics

Conventional PE films have been used for crop protection and enhancement for several decades, but owing to the persistence of these films after their service life is over, problems with harvesting and planting equipment occur. Visual pollution (litter) is also a serious problem with film residues. The requirement for a controlled service life of several months up to a year or more for mulch and silage films followed by a rapid loss of mechanical properties is called for [34]. At the end of the crop growth and/or protection period, the film must disintegrate readily, and the molecular fragments should biodegrade readily in arable soil. Plastor, a commercial PE mulching film based on Scott–Gilead technology, contains iron dithiocarbamate which functions initially as an antioxidant to maintain mechanical properties throughout the growing season. At the end of that period, photo-oxidation to embrittlement occurs, and the film fragments strongly support microbial growth in the absence of any other source of carbon [1]. A variety of induction times can be obtained, and several agriculturally useful products [11,35,36,40] have met with widespread commercial success on the basis of this science. The Scott–Gilead technology is so versatile that it can be used in the production of two consecutive, fast-growing vegetable crops with the single mulching film timed to degrade as the second crop is being harvested [11,37,41].

Likewise, commercially viable, degradable PE mulch film can be based on the TDPA® technology developed by EPI Environmental Plastics Inc. In a comparison trial at the SAC Crichton Royal Farm in Scotland, TDPA®-PE film was evaluated against two other commercial products, with forage maize as the crop. All three films increased crop values but the TDPA® product showed the lowest costs per unit weight for dry matter, metabolisable energy, and starch. The crop protection/disintegration timing was also superior for the product developed by EPI. Products for agricultural applications based on EPI formulations are being developed and marketed by Ciba Specialty Chemicals, under the trade name Envirocare™. Details of a comparison between the results of laboratory experiments and field trials demonstrated [48] that successful results are obtained with mulch films containing Envirocare™ additives for different crops in different countries. Field trials are also running for solarisation films, small tunnel films, seedling bags and banana bags.

4.3. Compost bags

No laboratory-scale test has yet been devised that really duplicates the conditions in a commercial composting plant. This is unfortunate because, with such a procedure, it would be possible to identify materials suitable for inexpensive, one-way containers for the collection and composting of food and garden waste, indeed, of any organic matter in municipal solid waste. Oxo-biodegradable PE bags, with a prodegradant included in the additive formulation, meet all of the requirements including high wet strength. Compost bags produced using EPI's TDPA® technology were evaluated by Raninger (Loeben University, Austria) using the municipal composting plant of Vienna Neustadt. Detailed results have been published [49] but the overall results may be summarised as follows:

- The TDPA®-modified PE bags did not interfere with the biodegradation of the normal input to the plant – about 10,000 tons annually of mixed household and green garden waste.
- The TDPA®-modified PE bags underwent biodegradation during the composting operation.
- The resulting compost product, which contained particulate and partially biodegraded plastics, was premium quality material and passed all the usual ecotoxicity tests. These included seed germination, plant growth and organisms' survival (daphnia, earthworms) tests carried out in accordance with DIN V 54900-3, ON S 2200 and ON S 2300 national standards.

It is clear that heat generated microbially in composting is the ''trigger'' that causes oxidative degradation of the PE, and that this happens relatively rapidly because of the prodegradant. Molar mass decreases cause polymer embrittlement, mechanical stresses from windrow turning speed up PE film fragmentation, and polymer surface area increases. The microorganisms in the compost biodegrade the oxidised plastic at molar mass values at least as high as 40,000 [1], more rapidly as M_w values are reduced further. This is the two-stage process referred to earlier, and it seems to proceed at a rate comparable to that of naturally occurring plant material.

It is evident that oxo-biodegradable plastics based on polyolefins contribute to the amount and nutritive value of the compost because much of the carbon from the plastic is in the form of intermediate oxidation products, humic material and cell biomass [50]. This is in contrast to plastics, such as hydro-biodegradable polyesters that biodegrade at rates comparable to purified cellulose. At the end of the commercial composting process, all of the carbon from the latter has been converted to CO_2, so there is a contribution to greenhouse gas levels but not to the value of the compost (see Section 6).

4.4. Landfill disposal

Most packaging plastics and many other types of plastic items and containers are disposed off in landfills. The costs of collecting, cleaning and sorting all these post-consumer plastics are high, and the market for mechanically recycled plastics is limited, partly for this reason. Proper incineration of waste plastics would enable the recovery of most of the energy stored in them (polyolefins are excellent fuels) but modern incinerators are expensive and the ''NIMBY'' principle also applies [10]. It seems that waste plastics will continue to be sent to landfills where their inherent bioinertness could be an asset, except for the following considerations. Many waste materials (e.g. food wastes, garden wastes, paper) that are known to be biodegradable persist in the landfill environment for many years in spite of significant microbial activity therein. This is partly because so much of this waste is enclosed in bioinert, impervious plastic bags and wrappers which impede the flow of gases and liquids and reduce the possibilities for aerobic biodegradation. All landfills change from aerobic to anaerobic conditions at any given place as the depth of garbage above that place increases. There are several advantages to encouraging as much aerobic biodegradation as possible of the organic matter disposed off in landfills before anaerobic conditions develop. Conversion of the carbon in the waste to carbon dioxide instead of methane [10 (p. 75–6)] and rapid reduction of the waste volume in order to prolong the useful life of the landfill are two such advantages. There is much to be said, therefore, for using oxo-biodegradable polyolefins in virtually all plastic applications for which disposal in landfills is probable after use [51].

The situation for polyolefins with controlled degradability in a landfill environment may be summarised as follows. These materials must have the familiar excellent mechanical properties during use, but they must embrittle and fragment much more rapidly in landfill conditions after disposal than do ordinary PE bags and films. Initiation of oxidative degradation (peroxidation) is the result of heat generated microbially in landfills. Disintegration of these plastics follows molar mass reduction as a result of the mechanical actions (compaction, settlement) that occur during normal landfill operations. The fragmentation of the films and bags allows the vertical flow of liquids and gases which enhances the aerobic biodegradation of food and ''green'' garden wastes, paper and the like. PE films that have been manufactured using EPI's TDPA® technology have been evaluated in several independent trials, using landfills in Canada, China and England. Tensile and spectroscopic measurements clearly showed the oxidative and mechanical deterioration of these films in a matter of months, even during the winter [52].

A further application of oxo-biodegradable TDPA®-based PE is as a daily cover for the active face in landfill operations. In many parts of the world it is mandatory to apply a daily cover to minimise the spread of refuse, odour and microorganisms, and 15 cm of soil has often been used for this purpose. Such a cover is wasteful of space and hence expensive…., and it is increasingly common to use a PE film. In order to avoid the problems inherent with the landfilling of conventional packaging plastics (described above), EPI's Enviro®Cover [52] is being used in a number of countries as an inexpensive replacement for soil. As is required, the Enviro®Cover provides the necessary cover protection but undergoes relatively rapid peroxidation to embrittlement after about 12 months, or less.

4.5. Toxicity

It has been important to establish that nothing harmful to the environment is generated or left behind by the use and disposal of polyolefins with controlled environmental degradability. It should be noted that the additives used to promote peroxidation of oxo-biodegradable polyolefins do not alter the normal oxidation chemistry of these materials but only speed up the slowest (rate-determining) of the individual reactions. The intermediate and final products of oxidation remain the same as those from ordinary polyolefins. Peroxidation involves the incorporation of oxygen (in combination with the carbon and hydrogen of the as-fabricated polyolefins), embrittlement and reduction of the original article to powder. This powder is harmless to humans, animals and plant life [35,36] and molecular oxidation and breakdown continue ''until the polymer is ultimately returned to the natural carbon cycle as simple compounds such as water and carbon dioxide''.

Of all the ''disposal'' environments discussed above, that of commercial composting encompasses the most rapid environmental degradation because the temperatures are highest and the microbial activity is greatest. The compost product from the Raninger trial [49] would have contained a wide spectrum of intermediate products of oxo-biodegradation from TDPA®-PE, and this material showed no contamination or harmful effects in the following tests: ''heavy metals'', plant tolerance and propagules, cress, summer barley plant growth, daphnia, and earthworm. As a result of exposure to near-UV light as well as to moderate temperatures and significant microbial activity, oxo-biodegradable polyolefins are most affective in agricultural applications. Photo-biodegradable PE films based on Scott–Gilead technology are widely used as mulching films (Plastor™ in Europe; Plastigone™ in the USA). They have been used in the same fields for 15 years or more, and there has been no accumulation of the plastic or its degradation products [3]. Calculation has shown [35] that continuous use of Scott–Gilead mulching film (containing a nickel

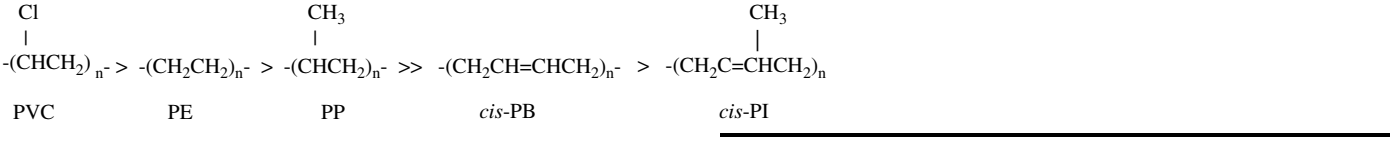
dialkyldithiocarbamate additive) for 500 years could increase the nickel content of the soil by one part per million, and the soil could contain up to 300 ppm to begin with. Moreover, it has been demonstrated [36] that water-soluble nickel corresponding to 180 years of continuous mulching had no effect on the ''assimilable'' nickel in the soil or on the amount of nickel incorporated in growing plants.

In the remaining applications (referred to earlier) of environmentally degradable polyolefins, the same degradation mechanisms prevail, the same peroxidation products are formed, and they are bioassimilated in the same way. Items made from oxo-biodegradable polyolefins that end up as litter will undergo primarily photo-initiated oxidation leading to biodegradable oxidation products. Likewise, packaging plastics made from such polyolefins that are discarded in landfills will (like Enviro®Cover daily landfill cover) oxidise abiotically as a result of the warmth generated by microorganisms. Film fragmentation has been observed to occur in less than a year. How long the biodegradation of oxidation products requires in soil or in landfills is not particularly important, but it is expected to be comparable to the times for paper, leaves, and other lignocellulosics. It has already been proven that no toxic residue formation occurs.

In the latter connection, there has been considerable negative publicity about the residual transition metal ions, often mistakenly referred to as ''heavy metals'' used to accelerate the abiotic degradation of the polyolefins. These are primarily carboxylates of Fe, Co, Ni and Mn, and are normally used at very low concentrations in the polymer. As discussed above, the agronomic effects of Ni have been particularly studied because of its reputation as a carcinogen. It has been demonstrated that, although small amounts of nickel are taken up by growing plants, this is not related to the concentration of nickel in the soil even at levels that could be reached if plastic films were used on the same soil for a century or more [34]. In fact the reputations of nickel and, to a lesser extent cobalt, were based upon studies of inhalation of dusts by miners. In practice, there is no evidence that aqueous nickel and cobalt salts are toxic. Indeed cobalt and manganese are widely distributed in drinking water and are required dietary supplements. They are taken in to the human diet through cereals, nuts and leafy vegetables and the plants receive these from the soils via water [37].

5. Scientific evidence for the oxo-biodegradation of hydrocarbon polymers

Carbon-chain polymers vary remarkably in their ability to resist peroxidation [53]. The following sequence shows some common commercial hydrocarbon polymers in order of decreasing oxidative stability.

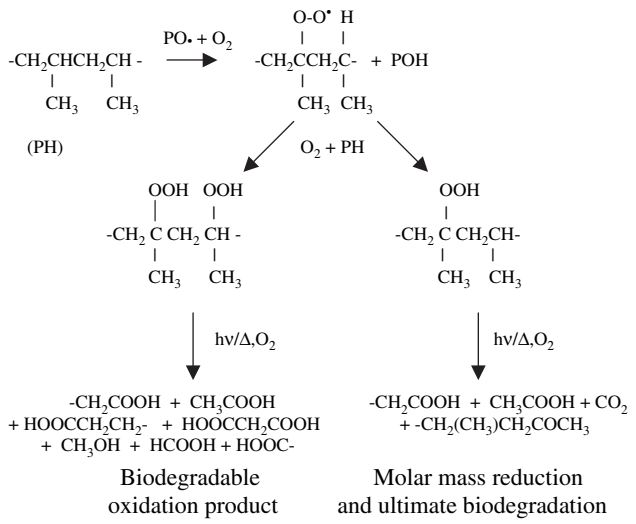


This sequence reflects the ease of hydrogen abstraction by peroxyl (see Section 3). Because of its ease of oxidation and loss of mechanical properties, the peroxidation of natural rubber (*cis*-poly(isoprene)) has been studied for many years and it is relatively recently that this process has been associated with its relatively rapid biodegradation and the inhibition of rubber biodegradation with the presence of antioxidants rather than with the polymer structure [27]. Contrary to the popular belief that synthetic polymers do not biodegrade like natural polymers, it has been shown [54,55] that naturally occurring *cis*-(polyisoprene) (NR) and synthetic *cis*-(polyisoprene) (IR) biodegrade at a similar rate in the presence of *Pseudomonas aeruginosa*. NR gloves were 26% mineralised in 6 weeks compared with 21% for IR gloves. This slight difference is probably due to the difference in the antioxidants used in the formulation [27]. Berekaa et al. [56] in a similar study showed that removal of antioxidants by extraction markedly increased the rate of microbial growth. It is clear, however, that there is no intrinsic difference between natural and synthetic polymers.

Less readily peroxidisable polymers do not biodegrade as rapidly as the polydienes in normal soils. Commercial nitrile and neoprene rubbers showed insignificant loss after 48 weeks and plasticised PVC showed mass loss (11.6%) that was due entirely to the biodegradation of the plasticiser and not to the polymer itself [57]. By contrast, NR gloves showed 54% loss of thickness after 4 weeks in soil at 25 °C and 94% mass loss after 48 weeks.

Abiotic peroxidation of the polyolefins (Scheme 3) gives rise to some vicinal hydroperoxides and this process is particularly favoured in the poly-α-olefins, such as polypropylene due to the susceptibility of the *tertiary* carbon atom to hydrogen abstraction via a hydrogen-bonded intermediate. A major proportion of the peroxidic products are hydrogen-bonded vicinal hydroperoxides that break down to small biodegradable molecules such as carboxylic acids, alcohols and ketones [4,28] as well as longer chain oxygen-modified breakdown products (Section 2), which oxo-biodegrade more slowly. The decomposition of the vicinal hydroperoxides is also facilitated by internal hydrogen bonding and the low molar mass products of this self-induced degradation are small biodegradable molecules such as acetic and formic acids.

In the case of the polyolefins, random chain scission is initially the dominant process (Scheme 3). However, some low molar mass oxidation products are formed via vicinal hydroperoxides even in PE [4,28]. The alkoxyl radicals formed by decomposition of the hydroperoxides contain weak carbon–carbon bonds in the α positions to the hydroperoxide groups, which lead to the formation of low molecular weight aldehydes and alcohols that rapidly oxidise further to carboxylic acids. These are biodegradable species, similar to products formed by hydrolysis of aliphatic polyesters and, as in the



Scheme 3. Formation and breakdown of hydroperoxides in polypropylene.

case of *cis*-PI, they are rapidly bioassimilated to give cell biomass (see below).

The conclusion from the above work, which has been reviewed in more detail elsewhere [29], is that the biodegradation of the polyolefins occurs by a combination of abiotic and biotic oxidation and that it is controlled by the rate of initiation of the abiotic peroxidation. The products of the abiotic peroxidation of the polyolefins are very similar to those formed in the abiotic hydrolysis of the aliphatic polyesters, such as poly(lactic acid), whether produced from biological resources or not and the two routes are complementary strategies to the biodegradation of synthetic polymers.

6. Science-based standards for biodegradable polymers

In the development of international standards for biodegradable polymers, it is generally considered essential that these are based on objective published scientific research in order to provide a ''level playing field for business'' [27,58,59]. This principle has so far not been in evidence in the International Standardization Organisations. In practice new standards for biodegradable plastics are almost entirely directed toward bioplastics that have achieved a high profile because they are derived from ''renewable'' materials. They are claimed to be more ''sustainable'' than polymers based on fossil fuels. This concept has been questioned [27,59] on the grounds that at least an equivalent amount of fossil resources is used during the manufacture of bioplastics as that required for the carbon content of the fossil-based synthetic hydrocarbons. Furthermore less than 10% of the fossil fuels used in energy production are used in plastics manufacture. The benefits of bio-based plastics, then, have to be made on the basis of their frequently claimed unique ability to be returned to the carbon cycle by biodegradation.

There is no question that some plastics made from natural resources are rapidly converted to carbon dioxide and water. However, there is no obvious ecological or practical advantage in rapid mineralisation. Rapid elimination of CO_2 to the environment is not considered by environmentalists to be an advantage because of its effect on the ''greenhouse effect''. Ideally, the carbon should be retained in the soil as a seed-bed for growing plants similarly to lignocellulose in the natural environment [60,61]. Furthermore, there is a general concern about the premature degradation of polymers, particularly when used in critical applications such as agricultural films, where their *reason d'etre* depends on their ability to resist the effects of the environment until they have fulfilled their intended purpose, which may mean that they have to be intact in contact with the soil for up to 12 months [3,37,41,62]. The behaviour of biodegradable polyolefins satisfies both of these requirements. Current progress in the development of standards for the biodegradation of polyolefins in Europe and America is discussed in the following sections.

6.1. Comité Européen de Normalisation (CEN)

CEN, the European Standards Organisation considers degradable materials under two different headings controlled by different Working Groups, TC 261/SC4/WG2 and TC 249/WG9.

6.1.1. CEN TC 261/SC4/WG2: Degradability and organic recovery of packaging and packaging waste

As the name implies, the mandate of this Working Group is not limited to plastics since it also embraces wood products, notably paper and cardboard. The remit of WG2 is primarily the recovery of packaging materials through composting. Other Working Groups of TC 261/SC4 are concerned with waste minimisation, mechanical recycling, energy production, etc. which in principle have to be regarded as alternatives to and in competition with composting as a means of recovering benefit from waste [62].

As indicated above, the primary target for compostability legislation has so far been the bioplastics (hydro-biodegradable plastics) because of their ''green'' image. The primary standard governing composting is EN 13432:2000 *Packaging – Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for final acceptance of packaging*. This embraces the following essential criteria

1 *Characterisation*: Identification of packaging constituents, dry solid content, ignition residues, and hazardous metal residues.
2 *Biodegradability*: 90% of the total theoretical CO_2 evolution in compost or simulated compost in 6 months.
3 *Disintegration*: Not more than 10% shall fail to pass through a >2 mm fraction sieve.
4 *Compost quality*: No negative effects on density, total dry solids, volatile solids, salt content, pH, total nitrogen, ammonium nitrogen, phosphorus, magnesium and potassium. Ecotoxicity effects on 2 crop plants.
5 *Recognisability*: ''Must be recognisable as compostable or biodegradable by the end user by appropriate means''.

Of these, criterion 1 is intended to identify potentially toxic components and 3–5 are to facilitate the commercial interests of the composting industry and are concerned with subjective judgements associated with the understanding of how normal commercial plastics behave. The main problem from a scientific standpoint is criterion 2, which utilises a biometric test derived from earlier ISO standards, originally intended to demonstrate the short-term biodegradability of detergents in aqueous media (ISO 14851, ISO 14852). Although this may be an appropriate test for water-soluble plastics that end up in a sewage plant, it has been strongly criticised by the European Association for the Co-ordination of Consumer Representation in Standards (ANEC) on the grounds that it really has nothing to do with composting [63]. Nature deals with its voluminous lignocellulosic wastes in quite a different way. It is also quite clear from the data presented in Sections 4 and 5, that the CEN ''biodegradability test'' is not compatible with the EU ''Waste Framework Directive'' 1991, [64] which defines ''recovery'' of materials as:

''Recycling/reclamation of organic substances … use as fuel to generate energy and spreading on land, resulting in benefit to agriculture or ecological improvement, including composting and other biological processes''.

However, if 90% of the total theoretical CO_2 were evolved during the composting operation in 6 months, the residue would have minimal value as a soil improver and would contribute almost nothing to the ''land carbon sink''. This is an important concept that has been highlighted in a number of documents from scientific organisations [65–68]. The following statement [68] emphasises the importance of organic carbon to the fertility of soil.

''Organic matter maintains a central role in soil function, in its fertility and its ability to hold water and to diffuse pollution. Moreover, it is the organic matter in soil which holds its carbon and enables it to act as a carbon sink''.

The sequestration of carbon in the soil is equally important in the context of mitigating global climate change by minimising the release of CO_2 to the environment [65,67]. Consequently, slow release of carbon to the soil as microbial biomass, which acts as a nutrient for growing vegetation, is clearly the more ecologically acceptable option than rapid conversion to CO_2 [27,29,41]. Complete mineralisation of plastics is favoured by parts of the composting industry because it provides a convenient means of disposing of packaging wastes rapidly to the environment. However, it is not ''recovery'' as defined in the Directive and in practice nature does not dispose of the enormous quantities of lingocellulosic wastes in this way. As discussed in Section 5, cellulose is stabilised by association with lignin and the slow biodegradation of natural lignocellulose serves as a model for the disposal of man-made wastes. Moreover, EN 13432 does not validate wood products as biodegradable since they do not comply with the rapid mineralisation requirement. This fact has been rationalised in retrospect [41] on the basis that, because lignocellulose is a natural product, it is not necessary to require that it must mineralise within 6 months. As seen earlier, there is no basic distinction between the biodegradation of natural and synthetic polymers (Section 5) and any distinction on grounds of origin are scientifically meaningless [29].

6.1.2. CEN TC 249/WG9 Characterisation of biodegradability

This Working Group is concerned with non-packaging applications of plastics. Because the range of applications of biodegradable plastics in the environment is so wide, they may terminate in quite different environments. For example agricultural products remain on the soil as litter after use for a relatively short period and terminate in the soil along with nature's litter. This is very different from biodegradable body bags, which are not intended to be exposed to the outdoor environment and which rely entirely on sub-soil bacteria to both initiate and terminate biodegradation. This is a long-term process, which unlike mulching films and tunnels that are required to disintegrate sharply to match the requirements of the farmer, there is no specified limit to the initiation or ultimate biodegradation of body bags.

A second application that requires a different time-scale again is for products that end up in sewage systems where disintegration and biodegradation must take place in a very short time to avoid clogging of pipes, etc. Products that comply with the rapid mineralisation test outlined in EN 13432:2000 are well suited to select materials that are required to be substantially biodegraded over a period of a week in a sewage plant. However, they are not at all suitable for plastics mulching films and protective tunnels or silage films, plant pots etc., which normally require a ''safety period'' in use in a biological environment of up to 12 months. Other applications of polyolefins, for example in baler twines, agricultural packaging or silage films may require an even longer induction period before disintegration commences [35–37,41].

The present proposal is to limit the scope of each standard to a single industrial sector. A standard for ''Biodegradable plastics materials suitable for manufacturing mulch films for agriculture'' has been proposed as a commercial priority [69]. However, although litter from mulching films, controlled release fertiliser capsules and related products can be classified as ''socially beneficial'' because of its benefit to the farming industry, it ends up in the same environment as ''anti-social'' litter from animal feed bags, fertiliser sacks, silage films and baler twines that end up as litter in the countryside. Similarly, litter from the shipping industry that terminates on the seashore in remote areas cannot be collected and recovered economically for more conventional recycling procedures. Generally biodegradable social litter is based on the same technology as biodegradable anti-social litter and there is no obvious reason why the appropriate standard should not be designed to cover both.

Plastics on soil are subjected to two synergistic influences: light and heat. The envisaged protocol for oxo-biodegradable litter should then utilise pre-treatment in a typical weatherometer in which both heat and UV light are generated. A filtered mercury arc developed by Professor Jacques Lemaire at the

University of Clermont-Ferrand has been found to be satisfactory for this purpose, but other standard weatherometers such as the xenon arc may also be adapted to simulate exposure on soil. In the draft standard it is envisaged that this pre-treatment will be optional if bioplastics are not light activated.

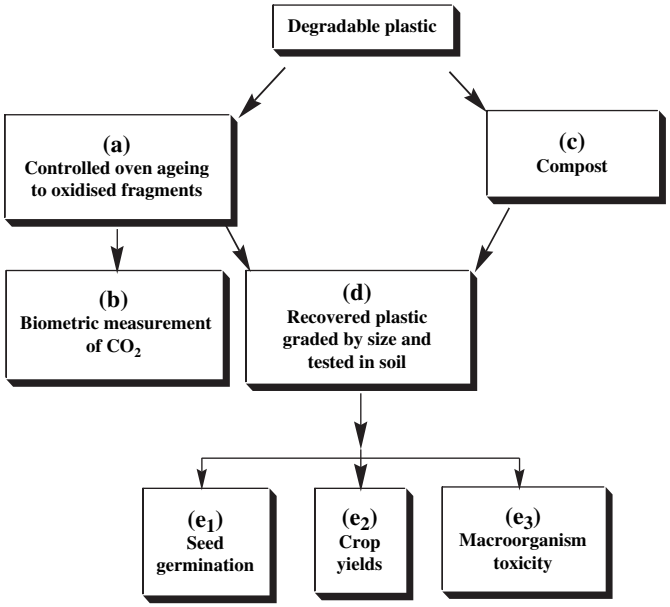
7. British Standards Institution

7.1. BSi PKW/0: Packaging and the environment

This committee is concerned with the environmental impact of packaging and its recovery. It is clear from the work described in the last section that oxo-biodegradable plastics cannot and indeed should not comply with rapid mineralisation tests without peroxidation after use, leading to biodegradable oxidation products. Moreover, it would be counterproductive if they did so, since their mechanical properties have to be maintained during their service life before disintegrating and biodegrading. These attributes have been considered by BSi PKW/0, the UK ''mirror group'' of CEN TC 261/SC4/WG2 [70]. It is proposed that, since hydrocarbon polymers are quite different from the materials covered by CEN TC 261/SC4/WG2, oxo-biodegradable polymers should be subjected to the same environmental influences experienced by plastics during composting (i.e. 60–70 °C in the presence of air). In practice, this transforms the polymer to a hydrophilic material that supports microbial biofilm formation. It is standard procedure for polymer technologists to apply accelerated ageing and weathering tests to polymers to predict their service life and this procedure must then precede conventional biometric measurements in order to replicate the complete life cycle of the plastic. This proposal is outlined in Scheme 4 [70]. Recent published work by Jakubowicz [7] has shown that oxo-biodegradable polyethylene films subjected to 70 °C undergo over 60% conversion to carbon dioxide in just over 6 months. Independently, Chiellini et al. [6] showed that after relatively mild thermal oxidative conditions (55 °C) oxo-biodegradable polyethylene was substantially converted to CO_2 within 18 months when incubated with both soil and with mature compost and extrapolation of result so far obtained suggest that this will be complete within 3 years. This time is actually rather shorter than the time required for the mineralisation of straw on soil [71]. The carbon content of the polyolefins cannot in their nature be converted to any toxic carbon compounds since CO_2 is the only carbon end product. The purpose of ecotoxicity tests outlined in Scheme 4 is to establish that plastics residues in soil do not interfere with the germination and growth of plants or migrate into the soil environment.

8. American Society for Testing and Materials (ASTM)

ASTM is a large organisation focused on establishing ''voluntary full consensus standards for materials, products, systems, and services by providing a forum for producers, users, ultimate consumers and those having a general interest''. It began to consider biodegradable plastics following the ill-advised introduction in the 1980s of starch-filled polyolefins as supposedly biodegradable and compostable. Since such materials were neither, ASTM requested its research arm, the Institute for Standards Research (ISR) to conduct research which could and did provide the basis for a *Standard Specification for Compostable Plastics* – ASTM D 6400-99. Over a 6-year period, the ISR investigated the requirements with participation from industry, government and academe. A major element of this program was a comparison of the results from laboratory-scale, pilot-scale and full-scale composting trials. A fundamental tenet of the work was that ''the only direct measurements of biodegradability are measurements of mineralisation, the conversion of carbon from the test



Scheme 4. Biometric and ecotoxicity evaluations for oxo-biodegradable polymers [70].

substance into gaseous carbon: CO_2 in aerobic processes or CO_2 plus CH_4 in anaerobic processes'' [72].

The emphasis in the laboratory-scale test was on the biometric measurement of the conversion of carbon to carbon dioxide, a test (as noted in Section 6.1) that derived from a test for the biodegradability of detergents in water treatment situations. This commonality between the approaches used by CEN and ASTM is not surprising in view of the continuing liaison between the two organisations. Among the important results of the ISR investigation was the finding that the laboratory-scale test was more conservative than the pilot-scale test which in turn was more conservative than the full-scale test [73]. In other words, the laboratory-scale test will ''fail'' plastics that actually biodegrade in full-scale composting.

Under the jurisdiction of ASTM D20 on plastics, Subcommittee D20.96 on Environmentally Degradable Plastics has produced three standards that are immediately relevant to the evaluation of degradable plastics: D 5338-98 *Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions* (originally published as D 5338-92); D 6002-96 *Standard Guide for Assessing the Compostability of Environmentally Degradable Plastics*; and D 6400-99 (re-approved in 2004) referred to above. Careful consideration of all three of these publications leads to the conclusion that a plastic which yields not less than 60% of its carbon as carbon dioxide in an incubation flask up to 5 L in volume at a temperature that may be kept at 58 °C over a period of up to 180 days may be considered to be biodegradable and compostable. The reader is directed to the standards for a full account of how the testing must be performed, and reported. The ASTM testing protocol does indeed identify plastics and other polymers, primarily hydro-biodegradable polymers, that can meet the designated criteria, although many of these do not biodegrade solely as a result of microbial activity.

Criticisms of the arbitrary assertion that only those plastics that meet the requirements spelled out in D 6400-99/D6002-02/D 5338-98 can be considered to be compostable tend to centre on the following facts: (1) this testing protocol requires a high rate of mineralisation that is actually a disadvantage in composting; (2) the protocol does not reproduce actual commercial composting conditions in regard to temperature, and microbial population profiles; (3) the positive control specified in D 5338 is purified cellulose, which is neither a naturally occurring substance nor a plastic; (4) no account is taken of the amount of carbon that is converted to biomass although this is an important product of biodegradation. ASTM's ISR recognized that the laboratory-scale test is more conservative than full-scale composting but the former is still the mandated requirement for compostability. This, in spite of the recognition by Subcommittee D20.96 that biodegradation processes, the conversion of carbon in materials into carbon dioxide by microorganisms in the environment, are expected to continue long after the compost has passed the curing stage and been applied to the soil.

There is widespread recognition that there is a legitimate requirement for a method to evaluate properly oxo-biodegradable plastics, since to date neither CEN nor ASTM has published standards that do that. Subcommittee D20.96 (now referred to as the Subcommittee on Biodegradable Plastics and Biobased Products) produced D 6954-04 with the title *Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation*. This new Standard Guide, approved and published in May 2004, ''uses a tiered, criteria-based approach to assess the consecutive oxidation and biodegradability of plastic products and ecological impacts in defined applications …. The tiered approach is chosen in the laboratory for convenient separation of oxidative degradation, biodegradation and ecological impact stages even though in the real world all three are likely to be concurrent rather than consecutive''. D 6954-04 is a useful addition to the ASTM Standards dossier dealing with degradable plastics since there are a number of important applications for biodegradable plastics for which those that meet D 6400-04 are unsuitable. During 2005, work was begun on preparing Standard Methods, based on D 6954-04 for landfill and litter disposal environments. Clearly, the search is not over for a laboratory-scale composting test that duplicates the actual conditions in full-scale composting. Perhaps the requirement will be met by simply reducing the rate at which carbon in the plastic is required to be converted to carbon dioxide. Time will tell.

Acknowledgements

We are grateful to Dr. Ignacy Jakubowicz, Professor Emo Chiellini, Dr. Andrea Corti, Dr. Graham Swift, Dr. P. Dole, Professor Jacques Lemaire, Dr. Anne-Marie Dulort and their colleagues for helpful discussions in the preparation of this review.

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May 3rd, 2018

Dear Mr Blainey,

Re: Response to the EU report on oxo-plastics, January 2018

I am writing to you as I am deeply concerned with the conclusions of the EU Commission's report[1] (16/01/18) and the subsequent proposal to ban oxo-plastics in the EU. I request that the proposal to ban oxo-plastic be retracted due to conclusions drawn from my own research outlined below.

Scientific Research at QMUL

I am a research scientist at Queen Mary, University of London, a member of the Russell Group of Universities and I have over 20 years' experience in the fields of biochemistry and microbiology. Over the last three years, together with a team of chemists and geobiologists, we have conducted a range of microbiological and biochemical tests to investigate the molecular mechanisms of plastic and polymer biodegradation.

Firstly, we have discovered that many of the testing methods used to date are insufficient to fully assess biodegradation and bio-toxicity[2,3]. Consequently, any previous conclusions reached on the bioavailability of any form of plastic do not give the full picture regarding the efficacy, environmental and biological impact of any part of the degradation process.

Importantly, we have applied our methods and compared the biodegradation of LDPE and oxo-LDPE in a fully defined and sealed environment by a bacterial species typical of a marine or a soil environment. Under these conditions we have observed significantly higher rates of carbon assimilation as a result of microbial activity once oxo-LDPE has undergone some degree of ageing[2]. Abiotic degradation of plastic causes a significant drop in the molecular weight of the oxo-polymer that is not observed for conventional LDPE. The oxidation of the polymer also makes the molecule more readily accessible for microbial mediated enzyme activity. Once biodegradation of a long carbon-hydrogen chain has begun there is no reason to believe that assimilation would not continue to occur until all the material has been consumed by the micro-organisms. In the laboratory, biodegradation is not expected to proceed as quickly or as fully as it would in the open environment[4]

[1] EU: *The impact of the use of oxo-degradable plastic, including oxo-degradable plastic carrier bags, on the environment* (2018).
[2] This work is currently undergoing peer review prior to publication in a scientific journal.
[3] Castro-Aguirre, E. *et al*. 2017. Insights on the aerobic biodegradation of polymers by analysis of evolved carbon dioxide in simulated composting conditions. *Polym. Degrad. Stab.* **137**, 251-71
[4] We have just begun testing plastic with environmental cultures and expect this work to be completed by the end of the year.

since the plastic is the only source of carbon and other nutrients cannot be replenished. Additionally, plastic in the environment has been shown to be colonised by many microorganisms[5], and not, as we have tested, a single species. Nonetheless, we clearly observed higher rates of oxo-plastic consumption compared to LDPE.

Further to my own research, I herewith include my direct response to several major features raised in the EU report that I urge be re-evaluated.

Addressing EU report

1. Research and science

The EU report states that experiments on oxo-LDPE are carried out "over too short a time span" and "give no conclusive evidence". This data will be forthcoming, as I have presented here, but rigorous, responsible, cross-disciplinary research of <u>any</u> type of plastic be it bio-based, biopolymer, oxo- or LDPE is costly and slow. To date, tests on oxo-plastic only compare against LDPE, where oxo-LDPE fares better. There are very few independent studies that subject all forms of plastic to the same conditions simultaneously. Until this has been carried out, there is no conclusive evidence to present any type of plastic as having a greater environmental impact.

I am troubled by the apparent desire of the EU Commission to discredit a single type of modified plastic; it does not send the positive innovative message that is needed. Further, the EU report heavily cites a single author that is dismissive of primary scientific sources[6]. Academic publications are subjected to severe scrutiny during the peer review process; provision of plastic from a company must be stated but does not force the scientist to present only data supporting a particular industry.

2. Fragmentation of plastic

Micro and nanoparticles exist in the open environment. They are a product of the breakdown process of LDPE released over the last 50 years. There is no technology available to remove it, though there is evidence of certain bacteria that have evolved to consume it[7]. These tiny pieces of plastic are part of a transitory phase during the disintegration of the polymer prior to inclusion in the carbon cycle. The EU report clearly acknowledges that oxo-plastic undergoes an accelerated rate of fragmentation, which could reduce entanglement and catastrophic ingestion by higher organisms. However, what has been omitted is that the oxo-plastic additive catalyses the depolymerisation of the primary carbon chain that makes a plastic bag. Not only is the physical plastic bag breaking down, but the long polymer hydrocarbon chain is oxidised and reduced in size, termed abiotic degradation. The lower molecular weight organic compounds are more readily assimilated by microorganisms as the molecules start to resemble naturally occurring compounds such as fatty acids[8]. I explained this directly to Commission officials in Brussels on 30th November 2017 as I wanted them to understand this fundamental point. I am concerned by the omission of this evidence from the Commission's report.

There is no evidence that standard LDPE undergoes any oxidation. Indeed only macroscopic and not molecular degeneration is observed. It is noteworthy that bio-based LDPE differs from LDPE only in the source of the carbon that comprises the backbone (coming from sugar cane rather than oil).

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[5] Dussud, C. *et al.* 2018. Evidence of niche partitioning among bacteria living on plastics, organic particles and surrounding seawaters. *Environmental Pollution.* **236,** 807-816

[6] Ellen MacArthur Foundation. 2017. Oxo-degradable plastic packaging is not a solution to plastic pollution and does not fit in a circular economy. Endnote 6. Less than 10% of references are peer reviewed scientific studies.

[7] Yang, J. *et al.* 2014. Evidence of Polyethylene Biodegradation by Bacterial Strains from the guts of Plastic-Eating Waxworms. *Environmental Science and Technology.* **48** (23). 13776-13784

[8] Kawai, F. *et al.* 2004. Comparative study on biodegradability of polyethylene wax by bacteria and fungi. *Polym. Degrad. Stab.* **86,** 105–114

Consequently, bio-based LDPE degrades in the exact same manner as LDPE *i.e.* slowly. Thus bio-based LDPE is not a better alternative than LDPE or oxo-LDPE. However, it is not included in the reference to ECHA.

3. Biodegradation in the marine environment

Previous reports[9] have attested to the lack of evidence for biodegradation of oxo-LDPE in the marine environment. There are no standards for any type of plastic under these conditions. We are working hard to address the lack of rigorous and non-polluting testing methods and have demonstrated, in the laboratory, that oxo-LDPE can be assimilated by bacteria commonly found in the oceans. I would find it irresponsible to impose powerful legislation with the little scientific data currently available.

4. Plastic in the food chain

The report rightly raises concern regarding incorporation of plastic into the food chain. However, there is no evidence to suggest that this is unique to oxo-plastic and rather that such assimilation will occur for all forms of plastic, be it bio-based, a true biopolymer, oxo- or LDPE. This is not a reason to ban a single form of plastic. Further, no toxic effects of the degradation of the specific oxo-LDPE additive have been shown either in our experiments or when subjected to standard testing methods.

Conclusions

There is no doubt that the current rate of plastic accumulation is unacceptable and new policies to restrict our reliance on plastic are needed. However, we still have very little understanding of the biological and chemical mechanisms of plastic breakdown. Importantly, we have no evidence at this point that any current commercially available form of plastic has greater toxicity during the degradation process. Indeed, oxo-plastic has been shown to have a higher rate of degradation compared to conventional LDPE, which is the main cause of accumulated plastic waste and microplastics.

To this end, I am surprised that the EU are proposing to ban a product that is certainly no worse than the unmodified LDPE that is not subject to the same action. Legislating against a single form of plastic is not the way to resolve the accumulation of many forms of poly-hydrocarbon but actively goes against EU policies that call for redesign and innovation.

I implore ECHA not to propose a restriction and allow more independent, scientific research to be carried out.

Yours sincerely,

Dr Ruth Rose

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