OXO-BIODEGRADABLE PLASTICS ASSOCIATION

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Oxo-biodegradable plastics: Questions and Answers

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Introduction

Although oxo-biodegradable plastics were invented for use in packaging and in agriculture over 30 years ago, they had not until recently gained the popularity of bio-based plastics for the following reasons:

- Synthetic polymers are at present manufactured as by-products of petroleum for economic reasons and are not therefore "renewable". They were initially made from bioethanol and could be so again if the production of bioethanol was to become sustainable.
- Because the poyolefins are not made by nature, environmentalists assumed that there are no biological mechanisms for their biodegradation[1]. This ignored the fact that abiotic processes such as photo- and thermo-oxidation play a very significant role in environmental biodegradation In practise it has subsequently been shown that as manufactured (i.e. without the antioxidants required to provide environmental durability), they rapidly biodegrade in biotic environments and are bioassimilated in soil[2].
- Since the rate of peroxidation of oxo-biodegradable plastics by molecular oxygen is slower than the rate of hydrolysis of hydro-biodegradable plastics, the rate of biodegradation is also slower than that of most hydro-biodegradable (bio-based) polymers This has been found to be a valuable technological attribute in controlling the useful lifetime of packaging and agricultural plastics. Furthermore, it also has ecological benefits, since in biotic environments, the oxidation products, which are essentially the same as those produced form hydro-biodgradable materials, are rapidly absorbed into the ecosystem.

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[1] A.G. Sadun, T.F. Webster and B. Commoner for Greenpeace, Washington DC (1990)
[2] J.K. Pandey and R.P. Singhe, ***Biomacromoledules***, **2**, 880-885 (2001)

Q What are oxo-biodegradable plastics?

A The technical merits of the polyolefins and their blends with rubbers and are well-established commodity plastics, both in packaging and in engineering applications. Because of their scale of manufacture, they are also economical to produce and convert to a wide range of products. Biodegradability is enhanced by the incorporation of transition metal catalysts that accelerate their rate of oxidation in the environment at the end of their useful life by as much as 50 times compared with regular polyolefins. The main transition metal ions used, which are frequently and wrongly referred to by misinformed environmentalists as "heavy metals" are iron, cobalt and manganese. They are non-toxic and are widely dispersed in agricultural soils and in food and water. They are trace elements which are actually required in human and animal nutrition[3]. The pro-oxidant activity of the transition metals is controlled during processing and subsequent use by thermal antioxidants and in the outdoor environment by light stabilisers.

Q Is it true that the use of oxo-biodegradable plastics leave residual plastic particles in the soil?

A Oxo-biodegradable plastics, after modification by environmental oxidation, are no longer plastics. Before oxidation, they are hydrophobic and cannot support the growth of micro-organisms, After exposure to environmental influences (oxygen, light and/or heat) they act as nutrients for bacteria and fungi, which colonise the surface of the oxidised plastic[4]. The average molecular weight of polyolefins that have been exposed to ageing and weathering determines their subsequent rate of bioassimilation. However, the molecular range varies between small molecules such as acetic acid and formic acid in the surface of the polymer. These are rapidly bio-assimilated by micro-organisms but the larger molecules (up to 40,000 Daltons) require further oxidation before they can be rapidly bio-assimilated. The oxidation is governed by the known kinetics of peroxidation, which may be abiotically or biotically promoted. In a homogenous polymer, this process continues from the surface at the same rate until all the polymer has been oxidised. In the case of films, oxidation leads to rapid fragmentation and increase in surface area of the oxidised polymer exposed to the micro-organisms until the original carbon in the polymer has been completely converted to biomass and carbon dioxide.

The process described above is increased by accelerated ageing (increasing the testing temperature) and molar mass reduction can be predicted by means of the Arrhenius relationship[5]. This allows the rate at accelerated ageing to be related to that of the same process at ambient temperatures. The evidence shows that over 60% mineralisation takes place in a laboratory test in two years, and complete bio-assimilation of oxo-biodegradable polyethylene will take up to four years. This is comparable with nature's wastes such as straw, which under the same conditions would take about 10 years to mineralise[6].

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[3] UK Food Standards Agency Expert Group on Vitamins and Minerals (2003), Risk Assessment.

[4] Bonhomme, A. Cuer, A-M. Delort, J. Lemaire, M.Sancelme and G.Scott, ***Polym. Deg. Stab.,*** **81**, 441-452 (2003)

[5] Jakubowicz , I , ***Polym. Deg. Stab***., **80**, 39-43 (2003).

[6] Janssen, S.L., ***Report of the FAO/IAEA Technical meeting***, 9-14 Sept., Pergamon Press (1963)

Q Is it true that oxo-biodegradable plastics cause pollution of the oceans and on the seashore?

A There have been many reports over the past 20 years of plastic wastes floating in the ocean currents and of consequent damage to sea mammals that ingest them by mistake as food. In other reports, mammals have become entangled in some forms of packaging and in particular by netting from fishing vessels. These plastics have not been identified but are made by the traditional procedures of the polymer industries. In spite of the Marpol regulations which prohibit the dumping of waste plastics in the sea, considerable quantities of durable detritus continue to be washed up on the seashores, even in remote areas where there is no almost no habitation. In a recent survey on the Isle of Skye in Northwest Scotland, it was found that almost all of the detritus came from shipping and in in particular from the fishing industry in the form of durable nets, ropes, oil containers and even plastic engine covers. None of these were oxo-biodegradable. If they had been they would not be there at all.

Recently there have been reports of plastic residues containing toxic substances at the bottom of the oceans. The chemical nature of these materials has not been identified, but again, they are unlikely to be oxo-biodegradable polyolefins since most of these materials float on the surface where they are rapidly oxidised under the influence of UV light and oxygen. As described above the polymer surface is rapidly bio-eroded by micro-organisms and the plastic continues to peroxidise on the surface of the sea until it is consumed. It seems likely that the dense residues that sink to the bottom of the sea are based on PVC. This polymer is not suitable for oxo-biodegradability since it is oxidised with the liberation of HCl, and toxic low molar-mass chlorine compounds are formed.

Q Can oxo-biodegradable plastics be composted

It is important to recognise that compost is an artificial man-devised process. Although composting involves biodegradation it is quite different from biodegradation in the natural environment. By contrast, tests for compostability are designed to satisfy the requirements of manufacturers of bio-based plastics

For example, International Standards for compostability, (e.g. EN 13432 and ASTM D 6400) require that the carbon in the polymer is "completely consumed" during the composting process. That is - converted to carbon dioxide, minerals and a small amount of dead-cell biomass in 180 days or less. However this is not the way in which nature converts its waste to valuable fertilisers.

In nature, lignocellulose, the most abundant biopolymer, is converted to low molar mass chemicals that are nutrients for micro-organisms. Expelling carbon to the atmosphere in 180 days provides no benefit to the natural environment but instead contributes to the "greenhouse effect". Most importantly, compost made in this way is not compliant with the EU Waste Framework Directive (1991) which requires that biological recovery is achieved by "Recycling/reclamation organic recovery of organic substances…by spreading on land resulting in benefit to agriculture or ecological improvement including composting and other biological transformation processes" Conversion of carbon to CO_2 by this definition is not "recycling, reclamation or recovery" but simply increases the "greenhouse effect"

The alternatives to the above - windrow and pile composts, like garden compost are not uniformly aerated. As in the case of landfill, they can produce methane, which is over twenty times more effective than carbon dioxide as a "greenhouse gas." Mechanical turning increases aeration but at the same time it reduces the temperature of the mass below that required to provide consistent sanitisation from pathogenic organisms. Full-scale industrial in-vessel composting plants avoid these difficulties since they normally operate at temperatures between 60^{o}C and 80^{o}C but are expensive to operate. Nature's prolific oxo-biodegradable lignocellulosic wastes do produce valuable composts,

Although oxo-biodegradable polyethylene bags have been satisfactorily composted in industrial composting facilities[5], they do not satisfy the artificial (90% in 180 days) time-scale. The deficiencies in this classification, as described in the previous sections, have been brought to the attention of CEN, ISO and ASTM. The composting standards were developed to match the bio-based plastics, and since bio-based plastics are more expensive than oxo-biodegradable plastics and cannot be re-used or recycled in the waste stream, the "bioplastics" industries rely almost exclusively on the above-mentioned international standards to gain acceptance of their products, and are therefore unwilling to consider science-based ecological arguments.

Q Do transition metals have adverse effects in the soil or in human nutrition?

A A risk analysis carried out by the UK Food Standards Agency[3] has shown that all the important transition metal ions used as catalysts of oxo-biodegradation are widely distributed in agricultural soils and taken up by the foods that humans eat, and in drinking water. Some of them, typically iron, cobalt and manganese are essential trace elements, all obtained from foodstuffs and drinking water.

For example, high concentrations of cobalt are found in fish (0.01 mg/kg), nuts (0.09 mg/kg), green leafy vegetables (0.009 mg/kg) and fresh cereals (0.01 mg/kg). Most of the cobalt ingested is inorganic. Fresh water concentrations of Co range from 0.001 to 0.01 mg/L. The mean population intake of Co is 0.012 mg/day. Cobalt is also included in some multi-constituent licensed medicines, at a maximum daily dose of 0.25 mg. Cobalt is an essential trace element, and Co deficiency has not been reported in humans (presumably because of its widespread availability from food and water).

Similarly, nickel is present in a number of enzymes in plants and micro-organisms, and in humans it influences iron absorption and metabolism. It is found in a variety of foods as ionic Ni, particularly in pulses and oats (0.18 mg/kg in miscellaneous cereals), and in nuts (1.77 mg/kg). Lower levels are found in water. Total intake of nickel by humans from all sources is up to 0.26 mg/day and

[5] G. Scott and D.M Wiles, ***Degradable Polymers: Principles and Applications***, 2nd Edition, ed. G. Scott, Chapter 13[5]

no potential high intake groups have been identified. The average intake from food and drinking water is 0.16 mg/day.

The amount of transition metal ions available to plants from common soils is very much greater than could be produced from degradable plastics in the soil and is much higher than can be absorbed by plants[8]. Particular attention has been paid to cobalt and nickel. However agricultural soils contain very high concentrations of cobalt oxide (up to 100 ppm) and nickel oxide (up to 750 ppm). Sandstone and limestone contain 90 ppm and 10-20 ppm of nickel respectively[9] and it can be calculated that in the 'worst case scenario', it would take 500 years to increase the nickel content of soil using typical nickel contents of degradable polyethylene mulching films by 1 ppm[8].

Q Do oxo-biodegradable plastics biodegrade in landfill?

A Sanitary landfill is essentially an anaerobic system. As already indicated, oxo-biodegradable plastics cannot biodegrade before being oxidised by atmospheric oxygen. Thus, in the surface layers of a landfill where, oxygen is available, oxo-biodegradable plastic bags disintegrate rapidly, releasing their contents and the oxidation products are rapidly scavenged by aerobic micro-organisms. However the deep layers are anaerobic, and there the residual oxo-biodegradable plastic particles remain inert and contribute to the land carbon sink[9]. Because they are present as small particles, they occupy much less space in the landfill.

Q Do biodegradable plastics interfere with recycling?

A Commercial biodegradable plastics fall into two distinct classes distinguishable by their biodegradation mechanisms.

1. Oxo-biodegradable Plastics

Oxo-biodegradable plastics have been in commercial use since the 1970s, and are based on commodity polyolefins, particularly polyethylene and polypropylene. Their technological performance during manufacture and use is indistinguishable from that of regular polyolefins, and their biodegradation is caused by an additive which promotes transition metal ion oxidation in the presence of atmospheric oxygen.

The length of the useful life of the plastic products is determined by antioxidants (processing stabilisers and UV stabilisers) contained within the additive, and the additive can be formulated so that the plastic product degrades according to whatever timescale is required.

Oxo-biodegradable plastics can be collected in the main polyolefin waste stream for recycling and are fully compatible with regular polyolefins.

[8] D.Gilead in ***Degradable Polymers: Principles and Applications***, 1st Edition, Editors, G.Scott and D.Gilead, Chapman & Hall (Kluwer), 1995, Chapter 10.
[9] A.Fabbri in ***Degradable Polymers: Principles and Applications***, 1st Edition, Editors, G.Scott and D.Gilead, Chapman & Hall (Kluwer), 1995, Chapter 11.

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If the new product to be made from recyclate is intended to be degradable, the process is quite straightforward, as a pro-degradant effect is actually desired. This applies particularly to closed-loop recycling in plastic factories, or where used oxo-biodegradable "back-of-shop" plastics (e.g. shrink-wrap and pallet-wrap) are sent back for recycling into more oxo-biodegradable products.

As polyolefins will always suffer a loss of properties during recycling, whether the recycling feedstock contains oxo-biodegradable plastic or not, the manufacturer using the recyclate to make a new product may need to add stabilisers, and/or further pro-degradant additive, to achieve the desired result, depending upon the use for which the new product is intended.

Similarly, if the new product to be made from recyclate containing oxo-biodegradable plastic has a very thick cross-section, (such as road cones, garden furniture etc), the process is straightforward. Again, whether the recyclate contains oxo-biodegradable plastic or not the manufacturer of the new product will need to add stabilisers to maintain the mechanical strength that would otherwise be diminished during the process. If suitably formulated, these stabilisers will neutralise any residual pro-degradant additive.

If the new product to be made from recyclate is a film intended for long-term use, such as a damp-proof membrane, the manufacturer of the new product should always add stabilisers to ensure strength and longevity, whether the recyclate contains oxo-biodegradable plastic or not. As already indicated, these stabilisers will neutralise any residual pro-degradant additive.

2. Hydro-biodegradable Plastics

This second class of biodegradable plastics are generally based on intermediates of biological origin derived from crops. Crop-based plastics were developed some 20 years after their oxo-biodegradable counterparts, and there are two sub-classes of different origins.

The earliest was poly (3-hydroxy butyrate), PHB, produced biologically from sucrose. This is an expensive product with a relatively low thermal decomposition temperature, which was partially overcome by varying the structure of the alkanoate structure (PHA). The second sub-group of hydro-biodegradable polyesters are the synthetic aliphatic polyesters, which are in some cases based on biological intermediates (e.g. poly(lactic acid), PLA).

Both sub-groups are physically incompatible with mainstream plastic wastes and even with commercial polyesters, due to their thermal instability.

Plasticised starch is a different type of bio-based plastic used in packaging. This material has acceptable initial properties but has poor durability due to hydrolysis in the presence of oxygen during use, and cannot normally be re-processed for use in the same application. Starch-based plastics hydro-biodegrade rapidly, but only in microbial environments, and they emit methane under anaerobic conditions. Like other bio-based plastics, they are not compatible with mainstream plastics used in packaging and cannot be recycled into useful secondary products.

Conclusions

Oxo-biodegradable plastics can be recycled and can be made from recyclate, but hydro-biodegradable plastics cannot.

The degradation of oxo-biodegradable plastics is controlled by stabilisers which inhibit abiotic oxidation. The same stabilisers control the performance of plastics during reprocessing and second use. No equivalent stabilisation procedure is possible in the case of hydro-biodegradable polymers, and such bio-based polymers are not normally physically compatible with main- stream polymers.

Q Can oxo-biodegradable plastics be used as fuel

A Unlike paper, cardboard and bio-based plastics, oxo-biodegradable plastics do not absorb water when in use or discarded. When they are incinerated with energy recovery, they produce as heat the carbon energy that stored in the polymer structure, which is identical to the fossil intermediates from which they were originally manufactured. In other words, the plastic is fully recovered as heat. By contrast the carbon in bio-based materials contains much less energy, and because they readily absorb water, they are less valuable as fuel.

Q what is the difference between "renewability" and "sustainability?

A Bio-based PE is identical chemically and technically to petro-based PE. Today bioethanol is produced from crops such as grain or sugar and it is becoming very obvious that this is not "sustainable" due to the ensuing competition for agricultural land and water with food supply and the consequent increase in the cost of foodstuffs. It is described as "renewable" but this is questionable in view of the large amounts of hydro-carbons burned during the growth and polymerisation of crops. Oxo-biodegradable plastics are made from a by-product of oil, which represents about 2% of each barrel of oil, which used to be wasted.