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Degradation of plastics, and microplastics formation

For the following reasons we are of the opinion that oxo-degradable plastics create microplastics, but oxo-biodegradable plastics do not.

1. Bioplastics and biodegradability

A major source of confusion is the difference between these terms: bioplastics, biodegradability, compostability, oxo-degradability and oxo-biodegradability. There is no universally-accepted definition of **Bioplastics** but in our view they are a large family of plastics sourced from biomass at the beginning of their life (bio-based), or metabolized into organic biomass and CO_2 at the end of their life, or both. **Biodegradable plastics** are a subset of bioplastics which can be hydro-degradable or oxo-degradable, and are then converted into water, carbon dioxide (CO_2) and biomass by the action of micro-organisms. As the biodegradability of a plastic lies in the chemical properties of the polymer —and not the source of the feedstock— biodegradable plastics can be either bio- or petroleum-based. **Compostable plastics** are a subset of biodegradable plastics, defined by the standard conditions required by the composting industry (temperature, humidity, etc) and the timeframe within which they are designed to biodegrade. All compostable plastics are biodegradable in a composting facility, but not all biodegradable plastics would comply with the composting Standards, usually because they may not reach 90% biodegradation within 180 days. **Oxo-*bio*degradable plastics (OBP)** are both bioplastics and biodegradable plastics, and consist of a conventional plastic containing a catalyst to reduce molecular weight and enable biodegradation. Conventional plastics which do not contain this catalyst are **oxo-degradable,** but they are not marketed as such. They quickly fragment into smaller and smaller pieces, called microplastics on exposure to weathering, but don't quickly break down at the molecular level like oxo-biodegradable plastics. The resulting microplastics are left in the environment until they are bioassimilated after a long period of time.

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2. Oxo-degradable -v- oxo-biodegradable

"**Oxo-degradation**" is defined by CEN TR15351 as "degradation resulting from oxidative cleavage of macromolecules." This describes ordinary plastics, which abiotically degrade by oxidation in the open environment and quickly create fragments, but do not become biodegradable except over a very long period of time "**Oxo-biodegradation**" is defined as "degradation resulting from oxidative and cell-mediated phenomena, either simultaneously or successively". This means that the plastic degrades by oxidation until its molecular weight is low enough to be accessible to bacteria and fungi, who then recycle it back into nature [1-6].

3. Oxo-biodegradable plastics

OBPs differ from oxo-degradable plastics in their manufacturing process. They contain masterbatches which prevent persistence in the environment by accelerating the oxidation of the plastic. These are often called pro-degradant, or pro-oxidative additives, but are more properly described as masterbatches, which contain not only the pro-oxidant catalyst but also anti-oxidant stabilisers, fillers, and a polymer-carrier. Depending on the formulation, they control the life of the plastic product for the appropriate time, and then cause degradation.

The biodegradation of all biodegradable polymers takes place due to the action of microorganisms such as bacteria and fungi. However, the process has two stages. In the case of OBP the first stage is the abiotic oxidation of the material promoted by the catalyst and further accelerated by UV rays/heat The second stage is biodegradation by microorganisms [1-6].

The mechanism of abiotic peroxidation of hydrocarbons has been extensively studied over the past 50 years. OBP was invented in the 1970s by Professor Scott and other polymer scientists [4,5] who had realised by then that polyethylene and polypropylene could cause an environmental problem if it escaped from the waste management processes and ended up in the open environment as litter. So, knowing that most of it would not be collected, they discovered that if they introduced into the normal polyethylene or polypropylene a tiny amount of a catalyst (which is usually a salt of manganese or iron) the plastic would not start to degrade in storage and would perform in exactly the same way as normal plastic whilst in use, but if discarded into the open environment it would rapidly become biodegradable, and be consumed by bacteria in the same way as nature's wastes.

There are several brands of masterbatches on the market, but the leading brand is d2w which usually contains manganese and/or iron salts, and is made in a wide range of formulations for different uses and climatic conditions. OBPs are made by incorporation of these masterbatches into traditional plastics such as Polyethylene (PE), and Polypropylene (PP) at the moment of extrusion into final products. They are not used for PET, PS, or PVC. The masterbatches cause a reduction in the molecular weight, and in a second phase the resulting residues undergo biodegradation. So, what the masterbatch does is to cause the molecular chains to be dismantled by oxidation so that the material is no longer a plastic and becomes biodegradable. The important thing is not the *size of the fragments*, but the molecular weight. Light and heat will accelerate the process, but it will continue even in dark, cold, conditions. Moisture is not necessary for oxidation and does not prevent it.

European Bioplastics (the trade association for the "compostable" plastics industry) has a position paper against oxo-biodegradable plastics, but we do not agree with it.

4. Peroxidation and bioassimilation of oxo-biodegradable plastics

As outlined above, it is crucially important 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 antioxidant stabilisers. It would be possible to make OBP so that it started to degrade immediately, but it would then have no useful life, and sustainability must in practice recognise commercial viability (i.e., cost and performance) and environmental acceptability.

Life-cycle assessments by Intertek have shown that OBP has a better LCA than the other materials used for packaging [7].

Oxo-biodegradable plastic is designed to be reused, recycled, and disposed of like normal plastic, but the masterbatch will make sure that if it gets into the open environment the molecular weight will reduce very rapidly so that it becomes biodegradable.

If the plastic has been taken to landfill, it has been responsibly disposed of and there is no need for it to degrade, but it will degrade if oxygen is present in the landfill.

It is NOT marketed for composting, although it will biodegrade in a composting facility. In fact although the type of plastic marketed as "compostable" does biodegrade, it does not convert into compost (as EN13432 and ASTMD6400 require it to convert into $C0_2$ gas) and it is therefore designed for a deliberate linear process and is not circular.

5. Microplastics

Most of the microplastics found in the environment are caused by the fragmentation of ordinary plastic when exposed to weathering. These fragments are very persistent because their molecular weight is too high for microbes to consume them and can remain so for decades. Recycling is also a source of microplastics [8]

Conditions in the environment cause the degradation of ordinary plastic articles leading to embrittlement and fragmentation on land or when floating on the ocean, in as little as 4-8 weeks [9] particularly when exposed to sunlight, erosion by mechanical forces, temperature-changes etc., Fragmentation will be accelerated by colorants and other impurities in the plastic.

Ordinary plastic and oxo-biodegradable plastic lose their strength and fall apart at about the same time when exposed to sunlight, but the fragments of ordinary plastic have a molecular weight which is much too high for biodegradation. The purpose of the oxo-biodegradable catalyst is to cause a rapid reduction in that molecular weight

Researchers and accredited test-houses have studied biodegradability of oxo-biodegradable plastics over two decades. For example in December 2021, Intertek tested an oxo-biodegradable plastic made with Symphony's d2w masterbatch according to ASTM D6954, and reported 92.74%

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biodegradation in 180 days. (It is not possible to find 100% in a carbon-evolution test, because some of the material converts into water and biomass). However, even if it had not biodegraded to that extent it would still be better than ordinary plastic, which would have created persistent microplastics but would not have biodegraded at all. The specimen also passed the tests for ecotoxicity, prohibited metals, and gel content.

In recent decades, biodegradable plastics have been investigated in outdoor weathering, soil and compost, sea water and freshwater, and under monitored experimental conditions, e.g., with identified microbial strains [10,11].

In summary it is clear that if plastic products are made with OBP masterbatch technology and get into the open environment intentionally or by accident, the molecular-weight of the plastic will reduce much more quickly and it will become a waxy substance which is no longer a plastic. It will then have become a source of nutrition for naturally occurring micro-organisms.

The European Chemicals Agency (ECHA) were asked to study this type of plastic in December 2017. They made a Call for Evidence, and they advised after 10 months that they were not convinced that it creates microplastics. We agree with them, and have seen no evidence that microplastics from this type of plastic have ever been found in the environment.

What is a microplastic?

According to ECHA [12] “Irrespective of their source, microplastics are persistent and universal pollutants. When products containing them are used, microplastics can be released to the environment where they stay for centuries, as they do not biodegrade.”

At Recital 11 of the draft Microplastics Act D083921/01 the EU Commission says “The Annex XV restriction report [13] proposed to exclude degradable (or water-soluble) polymers, and natural polymers that have not been chemically modified, as they do not possess the same long-term persistence and, therefore, do not contribute to the identified risk.”

Furthermore, when ECHA proposed a restriction on intentionally-added microplastics, they said that "it concerns only those that are consistent with the microplastic definition and relevant to the concern: less than 5 mm in size, solid, particulate, insoluble and non-biodegradable."

A small fragment of material is not therefore a "microplastic" if it is biodegradable.

This view is supported by the report by the Netherlands National Institute for Public Health and the Environment "Towards a definition of microplastics - Considerations for the specification of physico-chemical properties" [14] which says (p11) "The presence of plastics in the environment is of great concern because plastics are persistent." "From the perspective of the marine environment, microplastics that disappear quickly by natural processes (e.g. .. biodegradation to harmless degradation products), or microplastics that never reach the aquatic environment are not of concern."

Here are various statements about d2w plastics/OBPs degradation & possible microplastics formation:

Professor Ignacy Jakubowicz, one of the world's leading polymer scientists has described the process 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" [15].

This statement is correct. Pro-oxidant catalysts in the form of organic complexes or salts speed up the degradation process of polyolefins. These processes proceed through radical chain reactions, resulting in low molecular weight oxidation products (oxygen is introduced into the carbon chain in hydroxyl, peroxide, and carbonyl form)

Prof Heimowska and team from Gdynia Maritime University, Poland [16] studied and reported (2023) on the degradation process of d2w polyethylene under natural weathering, freshwater (pond), and water in laboratory condition for a period of 48 months. The extent of degradation was monitored by weight changes, mechanical properties, chemical functionality (FTIR) and surface morphology (microscopy). Natural weathering led to disintegration of the polymeric samples after 18 months, biodegradation to 81.6% after 39 months, and complete bioassimilation after 45 months.

The best practice to study the biodegradation of OBPs is to expose the plastic material to natural weathering conditions and monitor the abiotic degradation in the real environment. The biotic phase is then usually measured by carbon-evolution, which has to be done in the laboratory. However, the time required to achieve complete degradation and biodegradation can take years and is limited by cost factors. For this reason, accelerated laboratory tests are normally permitted by the Standards (eg ASTM D6954, BS 8472 etc) in order facilitate the introduction of a new material onto the market. For this purpose, accelerated UV laboratory weathering tests, with a fluorescent-UV or xenon-arc test chamber, are used to simulate the performance that a polymer material would have in the open environment under long-term weathering. See the evidence to the UK Government by Dr. Graham Swift, Vice-chairman of the Committee at ASTM responsible for Standard D6954.[17]

The following statement is made by Symphony Environmental Ltd. "The prodegradant catalyst in the d2w masterbatch accelerates oxidative degradation, but also – critically – removes the dependence of this process on sunlight so that, unlike conventional plastics or photo-degradable plastics, degradation will continue in darkness – even if buried - until biodegradability is achieved."

That statement is correct.

Vogt & Kleppe [18] studied accelerated weathering (UVCON) of polyethylene and polypropylene) with a pro-oxidant additive for various time (up to 120 hours), then transferred to dark thermal exposure (at 70 C) and the subsequent degradation during intervals up to 45 days was monitored by measuring elongation at break and tensile strength. The results demonstrate that the oxidative degradation, after initial light exposure, continues rapidly in the dark thermal conditions.

Symphony also say: "Professor Scott and other polymer scientists made it clear in their published work [4,5] that this type of biodegradable plastic will degrade and then biodegrade in the open environment very much more quickly than ordinary plastic, leaving no persistent fragments and no toxicity. Polymer scientists were themselves the authors of the standards for biodegradable plastics (ASTM D6954 and BS 8472 etc.) and it is not correct to say that there is insufficient evidence of biodegradability, or that there are no relevant standards." (Symphony Environmental Ltd)

That statement is correct.

The most frequently used standards [19] to confirm the biodegradability of oxo-biodegradable plastics are ASTM D6954 and BS 8472 They are based on a three-tier system divided into:

(1) Tier 1—Abiotic degradation: laboratory accelerated tests using UV light or heat in the presence of oxygen to promote oxidation and degradation of the polymer.

(2) Tier 2—Biotic degradation: the abiotically degraded polymer is further broken down by the action of microorganisms.

(3) Tier 3—Ecotoxicity: the final product of the abiotic and biotic degradation is tested for its toxicity on plants and earthworms.

There are many reports/articles available from researchers who investigated the possible formation of microplastics in soil but the most recent studies of oxo-biodegradable plastics [2, 9, 20] showed that the endpoint of the degradation/ weathering process **resulted in the formation of waxes**, and the authors indicated that **microplastics are not formed during the degradation** of the film containing the PAC additive. By contrast, the films without the additive showed a slower degradation and the authors considered that microplastics might therefore form during the erosion of the polymer.

The purpose of OXOMAR [10] was to investigate whether biodegradable plastics will fully biodegrade in a reasonable time in the marine environment, and to investigate whether biodegradable plastic or its by-products create any toxicity in the marine environment. It involved the complementary expertise of four independent laboratories (CNEP, LOMIC, ICCF, and IFREMER).

In their conclusion the scientists reported that "oxo-biodegradable plastics biodegrade in seawater and do so with a significantly higher efficiency than conventional plastics. The oxidation level obtained due to the d2w prodegradant catalyst was found to be of crucial importance in the degradation process. Out of the six-formulations tested, the Mn/Fe prooxidant was the most efficient, with no toxic effects under our experimental conditions. Biodegradability was demonstrated either by using the culture bacteria *Rhodococcus rhodochrous* or by a complex natural marine community of microorganisms."

Rose and coresearchers from Queen Mary University London [11] studied samples of LDPE and oxo-LDPE surface-weathered in sea water for 82 days, exposed to natural variations in sunlight and UV intensity, and tested the properties of the plastics. From the tests done in real time at Bandol on the coast of France it was observed that OBP degrades to low molecular-weight materials under natural conditions in water, and samples aged under those conditions were studied at Queen Mary University where the abiotically degraded plastic was presented as the only source of carbon available to the bacteria.

The samples were proved to be biodegraded by bacteria commonly found in the oceans, and separate samples were biodegraded by bacteria commonly found on land. The degraded plastic was also proved to be non-toxic to those bacteria. The researchers cannot be sure how long the plastic will take to biodegrade fully in the open environment, but say that it is not disputed by anyone that it will be many times faster than ordinary plastic when exposed under the same conditions in the open environment. They reported that it can be up to 90 times faster.

Though there is enough evidence on biodegradation of d2w plastics in the marine environment, the rate of physical and chemical (polymer breakdown and release of functional groups)

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degradation of OBPs can be slower than in open air/terrestrial environments There is a lack of information on the fate of OBPs when sunken into deeper waters, where factors relevant to degradation viz. light, heat and oxygen are limited. However the specific gravity of PE and PP is such that the plastic will float on the surface.

The degradation of plastic in the marine environment depends not only on abiotic parameters (e.g. light intensity/availability, temperature, pressure, current flow) but also on the fouling communities that colonize its surface. Reversible and irreversible cell attachment processes mediated by fouling organisms leads to biofilm formation and continuous accumulation of extracellular polymeric substances (EPS) on the plastic surface. However, biofouling [20] will have a more significant effect on conventional polymers, whose dwell-time in the environment is long, than with OBPs whose dwell-time is short.

No government in the western world has a policy for dealing with plastic waste which has escaped into the open environment, and cannot therefore fit into a circular economy. Their blind spot is that despite their best efforts a significant amount of plastic will continue to get into the open environment for the foreseeable future, which cannot be collected for recycling, composting, or anything else.

It must therefore be obvious that recycling cannot deal with the plastic which escapes into the open environment from which it cannot be collected. Nor can the type of plastic marketed as compostable deal with the problem, for it has to be collected and taken for composting – Biodegradable Plastics Association.

Oxo-biodegradable plastics are not marketed as compostable. They are also not marketed for anaerobic digestion, or degradation deep in landfill or ocean. However, if they do end up in landfill/marine, at or near the surface they degrade due to availability of oxygen and sunlight, and then biodegrade (by bacteria commonly found in soil and marine environments) in the open environment very much more quickly than ordinary plastic, leaving no persistent fragments and no toxicity. Though this degradation is much faster than a conventional plastic in the same time and place it will never be possible accurately to predict the duration of the biodegradation because conditions in the open environment are variable.

Although oxo-biodegradable plastic is normally used for low-value items which are not worth recycling, experts have found it to be compatible with recycling if anyone wanted to recycle it [21].

Oxo-degradable plastic has been banned in the European Union due to lack of evidence perceived by them of biodegradability in real-world conditions, associated with the risk of microplastic formation [22]. However, they have not clearly distinguished between oxo-degradable and oxo-biodegradable plastic and the legislation has therefore caused confusion. See also https://www.biodeg.org/eu-news/

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