Misleading Claims and Misuse Proliferate in the Nascent

Article contributed by

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Biodegradation takes place when microorganisms utilize carbon substrates to extract chemical energy that drives their life processes. The carbon substrates become 'food' which microorganisms use to sustain themselves. For this to occur, the carbon substrate needs to be transported inside the cell. Molecular weight is an important but not only criterion for transport across cell membrane. Factors like hydrophobic-hydrophilic balance, molecular and structural features also govern transport across the cell membrane. Under aerobic conditions, the carbon is biologically oxidized to CO_2 inside the cell releasing energy that is harnessed by the microorganisms for its life processes. Under anaerobic conditions, CO_2+CH_4 are produced. Thus, a measure of the rate and amount of CO_2 or CO_2+CH_4 evolved as a function of total carbon input to the process is a direct measure of the amount of carbon substrate being utilized by the microorganism (percent biodegradation). This is fundamental, basic biology and biochemistry taught in freshman classes and can be found in any biochemistry textbook. This forms the basis for various National (ASTM, EN, OECD) and international (ISO) standards for measuring biodegradability or microbial utilization of chemicals, and biodegradable plastics [1,2].

It would seem obvious and logical from the above basic biology lesson that to make a claim of biodegradability, all that one needs to do is the following: Expose the test plastic substrate as the sole carbon source to microorganisms present in the target disposal environment (like composting, or soil or anaerobic digestion or marine), and measure the CO_2 (aerobic) or CO_2+CH_4 (anaerobic) evolved. A measure of the evolved gas provides a direct measure of the plastics substrate carbon being utilized by the microorganisms present in the target disposal environment (% biodegradation). ASTM and ISO test methods teach how to measure the percent biodegradability in different disposal environments based, again, on the fundamental biochemistry described above.

It has been claimed by a few companies for quite some time that the addition of a low percent (about 1-5%) of proprietary additives in the form of a masterbatch to polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and other carbon chain polymers renders the carbon chain polymer completely (the claim has been 100%) biodegradable in both aerobic (composting, soil) and anaerobic (landfills) environments – that would mean that 100% of the polymeric carbon is completely utilized by microorganisms as measured by the evolved CO_2 (aerobic) or CO_2+CH_4 (anaerobic) – if this is true, then such data should be provided to substantiate the claim.

There are two classes of additives being marketed – 'oxo' and 'organic' which are sold as masterbatch concentrates. The 'oxo'

# of Standards Continues to BioPlastics Industry Space

additive is supposed to promote chain scission, thereby making the polymer small enough to be utilized by the microorganisms present in the disposal environment. The 'organic' additive initiates or promotes microbial attack, and that in some way triggers the microorganism to begin breaking down the carbon-carbon backbone chain polymer. Unfortunately, the scientific data and the literature do not support the actual claims being made in the market place. Many reports in the peer-reviewed literature include 'biodegradation' in the title; however, the meaning and context of the term is very broadly and loosely applied. Let's look at several examples:

Evidence of microbial growth on the surface of the polymer is reported as 'biodegradable' This is then extrapolated by manufacturers to claim that their product is 100% biodegradable, and some go onto claim that this can occur anywhere from 9 months to 5 years.

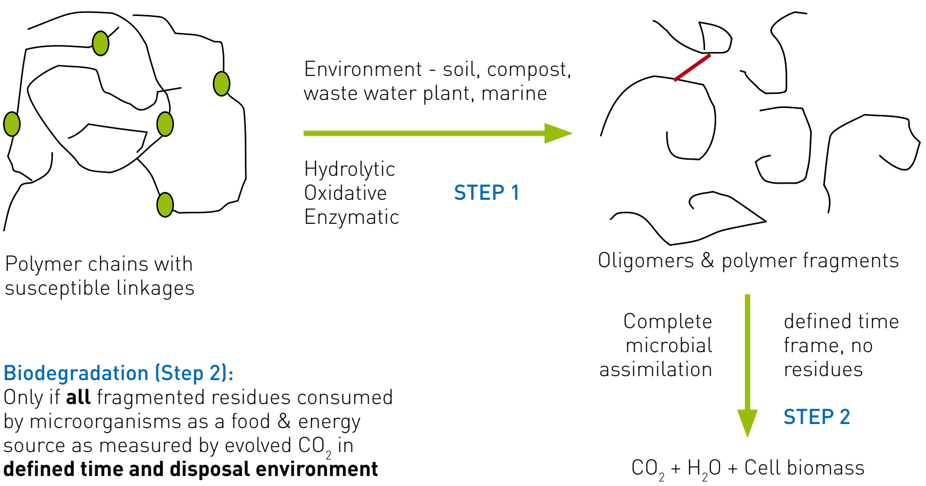
Some studies use the 'biodegradable' term to indicate that the PE samples were subjected to a biotic environment (soil, compost) as part of their experimental procedure. They go on to measure weight loss, molecular weight reductions, carbonyl index, mechanical property loss (films becoming brittle). Additive manufacturers reference these studies and extrapolate to stating that their product is 'completely (100%) biodegradable' in the environment based on weight loss and physical, chemical, or mechanical property loss. However the fundamental biology/biochemistry data showing carbon utilization by the microorganisms as measured by the evolved CO_2 (aerobic) or CO_2+CH_4 (anaerobic) is missing.

A peer reviewed Chem Communication journal (an established, well respected journal) paper [3] reported increasing the rates of biodegradation of polyolefins, by anchoring minute quantities of glucose, sucrose or lactose, onto functionalized polystyrene. A mere 2-12% weight loss and formation of carbonyl groups was evidence for biodegradation.

In another peer reviewed scientific journal paper, polyethylene and polypropylene were put in a composting environment after solvent extraction to remove the antioxidants present, and it was reported that PP lost 60% mass over six months, whereas low density polyethylene lost only 10%. It is well known that unstabilized PP will degrade in the environment. Professor Scott summarizes this in his book chapter as follows: *PP biodegrades much more rapidly than LDPE by mass loss in compost, and ethylene-propylene copolymers biodegrade at rates intermediate between polypropylene and ethylene. This implies that 60% of the PP carbon has been utilized by microorganisms present in compost*

What does Biodegradable Mean?

Can the microorganisms in the target disposal system (composting, soil, anaerobic digestor) assimilate/utilize the carbon substrate as food source **completely** and in a short defined time period?



as measured by evolved CO_2. However, no such data was available in the referenced text [4,5].

There are many more examples where physical, chemical, and mechanical property losses are used to claim 'biodegradability'. In some papers microbial colonization or biofilm formation is used to make claims of biodegradability. Weight loss, molecular weight reductions, carbonyl index, mechanical property loss, biofilm formation, microbial colonization do not confirm the microbial utilization of the polymeric carbon substrate, nor does it provide the amount of carbon utilized or the time to complete microbial utilization.

Misuse of Standards

There have been a number of standards developed by Standards writing organizations like ASTM, EN, and ISO [6]. They are summarized below:

Biodegradability under composting conditions

- Specification Standards ASTM D6400, D6868, D7021
- Specification Standards EN 13432 (European Norm)
- Specification Standards ISO 17088 (International Standard)

Biodegradability under marine conditions

- Specification Standard D 7021

Biodegradability Test Methods – ASTM Standards

- Compost D5338
- Soil D5988
- Anaerobic digestors D5511, ISO15985 (Biogas energy)
- Accelerated landfill D5526
- Guide to testing plastics that degrade in the environment by a combination of oxidation and biodegradation ASTM D6954

As discussed in the beginning all Standards for measuring biodegradability are based on fundamental biochemistry principles outlined earlier of carbon utilization by microorganisms as measured by the evolved CO_2 (aerobic) and CO_2+CH_4 (anaerobic). A specification standard provides the specifications for pass/fail and provides the basis for making claims for example claims of compostability (biodegradability under composting conditions) has to meet the ASTM, EN, or ISO specification standards.

There are also test methods to measure biodegradability under disposal conditions as shown above. Test methods teach how to measure biodegradability under the specific disposal environment. The results of such a test could be 0% or 100% biodegradability or somewhere in between. There are additive based products that claim to be in compliance with or pass ASTM D5526 or 5511. However, this meaningless unless one provides the results obtained from the test – then one can say that using ASTM D5511, I obtained xx% biodegradability.

ASTM D6954 is referenced in a number of oxo-degradable plastic claims. In an article published in this magazine's last issue, ASTM D6954 was identified as an acknowledged and respected Standard Guide for performing laboratory tests on oxo-biodegradable plastic. It is a generally accepted principle that Standards should be followed in its entirety, not modified to suit one's convenience or expediency or only certain parts of the standard followed and applied. It is a three tiered testing procedure - loss in properties and molecular weight by thermal and photooxidation processes and other abiotic processes (Tier 1), measuring biodegradation (Tier 2), and assessing ecological impact of the products from these processes (Tier 3). Key points of this Standard are:

- accelerated oxidation data must be obtained at temperatures and humidity ranges typical in that chosen application and disposal environment, for example, in soil (20 to 30°C)
- Tier 1 accelerated oxidation tests are not indicators of biodegradability and should not be used for the purpose of meeting the specifications as described in ASTM D 6400 and claiming compostability or biodegradation during composting
- For determining biodegradation rates under composting conditions, Specification D 6400 is to be used, including test methods and conditions as specified
- Complete mass balances are to be reported in Tier 1
- Tier 2 report must state the following: Extent of biodegradation (carbon dioxide evolution profile to plateau as per standards) and expressed as a percentage of total theoretical carbon balance
- Percentage of gel or other nondegradable fractions.

Basically, this means that pre-treatment of samples at 60-70°C in a dry oven is not acceptable. It also means that Tier 1 cannot be performed alone, but both Tier 2 and 3 must be completed. As indicated earlier, there are several references to meeting D6954 however no data is provided, except maybe Tier 1 data. However, claims of total biodegradability are being made. This is misleading and false.

The recent 2009 paper by Odeja et al. titled 'Abiotic and Biotic degradation of oxo-biodegradable polyethylenes' [7] is closest to the D6954 procedures. The oxo-biodegradable PE samples that were abiotically degraded in natural and saturated humidity for one year were biodegraded in a mixture of soil:compost:perlite (1:1:2) at 58°C for three months. The percent biodegradability as measured by evolved CO_2 was 3.61% (abiotic natural humidity) and 5.70% (abiotic saturated humidity). The percent biodegradability for samples weathered for one year in PP envelopes in compost at 58°C was 12.4%, and at 25°C was 5.4% after three months. Given this kind of almost negligible biodegradability data after one year weathering and subsequent exposure to an aggressive, biologically active compost environment for 3 months, it is surprising to note Professor Scott's claim that oxo products will totally biodegrade in the environment. The above study shows that a significantly large amount of the degraded plastics some of which could be microscopic would be released into the environment.

Environmental & Health Consequences

Making hydrophobic polyolefin plastics like PE unstable and degradable, and releasing them into the environment without ensuring that the degraded fragments are completely assimilated by the microbial populations in a short time period, has the potential to harm the environment and create human health risks. The fragments, some of which could be microscopic can transport through the ecosystem and potentially have serious environmental and health consequences. In fact, stringent 'REACH laws' governing the release of almost all chemicals (small molecules) are becoming the norm in Europe and other countries including Canada, require the chemical to be completely assimilated by microorganisms in the ecosystem if it is to be released into the environment.

In a recent Science article, Thompson et al. [8] reported that plastic debris around the globe can erode (degrade) away and end up as microscopic granular- or fibre-like fragments, and that these fragments have been steadily accumulating in the oceans. Their experiments show that marine animals consume microscopic bits of plastic, as seen in the digestive tract of an amphipod.

The Algalita Marine Research Foundation [9] reports that degraded plastic residues can attract and hold hydrophobic elements like polychlorinated biphenyls (PCB) and dichlorodiphenyltrichloroethane (DDT) up to 1 million times background levels. The PCBs and DDTs are at background levels in soil, and diluted out, so as to not pose significant risk. However, degradable plastic residues with these high surface areas concentrate these chemicals, resulting in a toxic legacy in a form that may pose risks in the environment.

Japanese researchers [10] have similarly reported that PCBs, DDE and nonylphenols (NP) can be detected in high concentrations in degraded PP resin pellets collected from four Japanese coasts. This work indicates that plastic residues may act as a transport medium for toxic chemicals in the marine environment

More recently the issues surrounding microscopic plastics release into the environment and causing environmental and human health problems was the subject of recent issue of the Philosophical Transactions (of the Royal Society) B titled "Plastics, the Environment, and Human Health" [11].

Conclusions

1. Incorporating biodegradability into plastics in concert with targeted disposal system like composting or anaerobic digestion offers an environmentally responsible end-of-life value proposition.
2. Weight loss and other physical, chemical and mechanical property reductions do not constitute a measure of the percent biodegradation, although they may help in the process.
3. Microbial assimilation/utilization of the substrate carbon as measured by the evolved CO_2 (aerobic) and CO_2 + CH_4 (anaerobic) is a measure of biodegradability.
4. Degradation or partial biodegradation is not an option as it may have potential environmental and human health consequences.
5. Complete biodegradation (microbial assimilation) of the plastic substrate in the targeted disposal environment (like composting) in a short defined time period is a necessary requirement.

Note: A complete list of references can be downloaded from www.bioplasticsmagazine.de/201001